ДОКЛАДЫ
АКАДЕМИИ НАУК СССР

Vol. 121, nos. 1-6
July-August 1958

PROCEEDINGS OF THE ACADEMY OF SCIENCES OF THE USSR

(DOKLADY AKADEMII NAUK SSSR)

Chemistry Section

IN ENGLISH TRANSLATION

CONSULTANTS BUREAU, INC.

ДОКЛАДЫ
АКАДЕМИИ НАУК СССР

Vol. 121, nos. 1-6

July-August 1958

PROCEEDINGS OF THE ACADEMY OF SCIENCES OF THE USSR

(DOKLADY AKADEMII NAUK SSSR)

Chemistry Section

IN ENGLISH TRANSLATION

C/b

CONSULTANTS BUREAU, INC.

Vol. 121, nos. 1-6

July-August 1958

PROCEEDINGS OF THE ACADEMY OF SCIENCES

OF THE USSR

(DOKLADY AKADEMII NAUK SSSR)

Chemistry Section

A publication of the Academy of Sciences of the USSR

IN ENGLISH TRANSLATION

Year and issue of first translation:
Jan.-Feb. 1956 vol. 106, nos. 1-6

Annual subscription	*$110.00*
Single issue	*25.00*

Copyright 1959

CONSULTANTS BUREAU INC.
227 W. 17th ST., NEW YORK 11, N. Y.

NOTE: The sale of photostatic copies of any portion of this copyright translation is expressly prohibited by the copyright owners. A complete copy of any paper in this issue may be purchased from the publisher for $5.00.

Printed in the United States

PROCEEDINGS OF THE ACADEMY OF SCIENCES OF THE USSR

Chemistry Section

Volume 121, Numbers 1-6 July-August 1958

CONTENTS

	PAGE	ISSUE	RUSS. PAGE
On the Reduction of Δ^3-Carene Oxide. Academician B. A. Arbuzov and Z. G. Isaeva	507	1	105
On The Interaction of Inhibitors of the Autooxidation of Hydrocarbons With Alkyl and Peroxide Radicals. K. I. Ivanov and E. D. Vilianskaia	509	1	107
Absorption Spectra of Molecular Complexes of 9-(p-Dimethylaminostyryl) Acridine With 10-Ethyl-9-(β-carbomethoxyethyl)Acridinium Iodide. V. A. Izmail'skii and L. D. Vishnevskii	513	1	111
A Triclinic Modification of Polythene. A. I. Kitaigorodskii and Iu. V. Mniukh	519	1	115
Synthesis of Methylferrocene. A. N. Nesmeianov, E. G. Perevalova, L. S. Shilovtseva, and Z. A. Beinoravichute	521	1	117
Synthesis of Silicon-containing Vinyl Ethers. Corresponding Member AN SSSR A. D. Petrov and S. I. Sadykh-Zade	523	1	119
Isotope Exchange of Hydrogen and the Reactivity of Methyl Derivatives of Nitrogen-containing Heterocycles in Condensation Reactions. T. I. Abramovich, I. P. Gragerov, and V. V. Perekalin	527	2	295
Use of the Polycondensation Reaction for the Preparation of Polymers. Corresponding Member AN SSSR V. V. Korshak, S. L. Sosin, and M. V. Chistiakova	533	2	299
A New Method of Synthesis of Cyclobutane Hydrocarbons. R. Ia. Levina, Iu. S. Shabarov, M. G. Kuz'min, N. I. Vasil'ev, and E. G. Treshchova	537	2	303
Fluorine-containing Organosilicon Compounds. Fluorine-containing Organosilicon Ethers. Corresponding Member AN SSSR A. D. Petrov, V. A. Ponomarenko, and G. V. Odabashian	541	2	307
Synthesis of the Methyl Ethers of Isomeric Chondrofolines, Chondodendrines, and Tubocurarines. V. G. Voronin, O. N. Tolkachev, and N. A. Preobrazhenskii	545	3	455
On Certain Regularities of Melting Point Changes in Homologous Series of Heterochain Polymers. Corresponding Member AN SSSR V. V. Korshak, and T. M. Frunze	549	3	458
On Substitution Reactions in the Methylene Unit of β-Ketoacetals. N. K. Kochetkov and E. E. Nifant'ev	553	3	462
On Some New Types of the Arbuzov Rearrangement. V. A. Kykhtin	557	3	466

CONTENTS (continued)

	PAGE	RUSS. ISSUE	RUSS. PAGE
On the Alkylation of Benzene and Its Homologs With Acetic Acid Esters of γ-Acetylenic Glycols. R. M. Lagidze, N. K. Iremadze, Sh. D. Kuprava, and Corresponding Member AN SSSR A. D. Petrov	561	3	470
Polymerization of Higher Dienic Hydrocarbons. I. A. Livshits and L. M. Korobova	565	3	474
The Stereochemistry of σ, π-Conjugation α-Chloromercuricamphenilone. Academician A. N. Nesmeianov and I. I. Kritskaia	569	3	477
Synthesis of Derivatives of 5-Mercaptoindole and 5-Mercapto-1-methylindole. Corresponding Member AN SSSR A. P. Terent'ev and M. N. Preobrazhenskaia	573	3	481
Dehydrogenation of n-Pentane and Isopentane in the Presence of Chrome-Alumina-Potassia Catalyst. Corresponding Member AN SSSR N. I. Shuikin, E. A. Timofeeva, and T. P. Dobrynina	577	3	485
On the Structure of the Products of the Reaction of Some α-Haloketones of the Carbocyclic Series With Triethyl Phosphite and With Sodium Diethyl Phosphite. Academician B. A. Arbuzov, V. S. Vinogradova, and N. A. Polezhaeva	581	4	641
Investigation of the Graft Copolymerization of Vinyl Chloride with Derivatives of the Methacrylic Series. A. A. Berlin, L. V. Stupen', B. I. Fedoseeva, and D. M. Ianovskii	585	4	644
Alkylation of Phenol With Acetylene at Elevated Pressure. V. L. Vaiser and V. D. Riabov	589	4	648
Infrared Absorption Spectra of Hydroxybenzylamines. L. A. Igonin and S. I. Bass	593	4	652
On the Action of Amines and Ammonia on Isoamylboron Dichloride. B. M. Mikhailov and T. K. Kozminskaia	597	4	656
The Stereochemistry of σ, π-Conjugation. Autooxidation in Rigid Allyl Systems. Academician A. N. Nesmeianov, K. A. Pecherskaia, A. N. Akhramovich, and L. M. Minakova	601	4	660
Some Data on the Kinetics of the Thermal Decomposition of Acetates of the Alkaline Earth Metals. A. M. Rubinshtein and V. I. Iakerson	605	4	664
Investigation of the Kinetics of the Polymerization of Isoprene Under the Influence of a Complex Catalyst. S. E. Bresler and M. I. Mosevitskii	609	5	859
Synthesis of 1-Benzyl-2-methyl-5-methoxytryptamine. A. N. Grinev, V. N. Ermakova, and Corresponding Member AN SSSR, A. P. Terent'ev	613	5	862
Catalytic Alkylation of n-Butane With Ethylene at High Temperatures and Pressures. N. M. Nazarova, Academician A. A. Balandin, and L. Kh. Freidlin	617	5	865
The Relation of Conjugation Characteristics to the Angle of Deflection of the Methoxyl and the Dimethylamino Groups Relative to the Plane of the Benzene Ring. P. P. Shorygin and Z. S. Egorova	621	5	869

CONTENTS (continued)

	PAGE	RUSS. ISSUE	RUSS. PAGE
Hydrocarbons of the Decalin Series in Mirzaani Petroleum. Kh. I. Areshidze and A. V. Kikbidze	625	6	1025
Investigation of the Structure of Unsaturated Nitro Compounds By Means of Their Raman Spectra. Ia. S. Bobovich and V. V. Perekalin	629	6	1028
Dipole Moments of Hexaalkyl Derivatives of Disiloxane. A. A. Gundyrev, N. S. Nametkin, and Academician A. V. Topchiev	633	6	1031
Condensation of the Acetal of β-Cyclocitral With 1-Ethoxyisoprene. Academician I. N. Nazarov and Zh. A. Krasnaia	637	6	1034

ON THE REDUCTION OF Δ^3-CARENE OXIDE

Academician B. A. Arbuzov and Z. G. Isaeva

In a report on the reduction of the oxides of α-pinene and Δ^3-carene [1], a few preliminary data were presented on the nature of the reaction products from the reduction of Δ^3-carene oxide in the presence of Raney Ni. It was shown that under these conditions, Δ^3-carene oxide is reduced to an alcohol of the composition $C_{10}H_{18}O$, which gives the crystalline derivatives: 3,5-dinitrobenzoate (m. p. 131-132°) and acid phthalate (m. p. 158-159°).

During a more detailed study of the hydrogenation of Δ^3-carene oxide, we found that, in addition to the alcohol mentioned above, two other products are formed – alcohols with the same general formula, $C_{10}H_{18}O$.

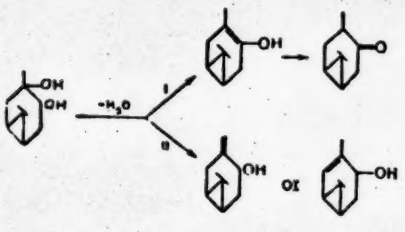
As already indicated, the first alcohol is apparently identical with the L-3-carol prepared by Kuczynski and Chabudzinski [2] by the action of powdered sodium in benzene on Δ^3-carene oxide and by the reduction of the isomerization product of Δ^3-carene oxide, L-3-carone, with sodium in ethanol.

The alcohol from the reduction of L-3-carone, which the authors gave a two-fold purification through the p-nitrobenzoate and the acid phthalate, had constants very close to those obtained by us for the alcohol purified through the p-dinitrobenzoate.

Literature data: b. p. 110°/20 mm, d^{20}_4 0.9516, n^{20}_D 1.4808, $[\alpha]_D = -67.1°$, acid phthalate m. p. 151.5° [2]; b. p. 106.5-107°/13 mm, d^{20}_4 0.9520, n^{20}_D 1.4822, $[\alpha]_D = -70.05°$, acid phthalate m. p. 158-159°. Thus, the alcohols differed a little only in the melting point of the acid phthalate; our crystalline derivative had the higher melting point.

When the product of the hydrogenation of Δ^3-carene oxide over Raney nickel was oxidized with chromium trioxide in acetic acid, the ketone $C_{10}H_{16}O$ was obtained, and this gave a quantitative yield of the semicarbazone with a m. p. of 201-202°.

According to the constants and m. p. of the semicarbazone, the ketone is identical with L-3-carone [2] – the product of the isomerization of Δ^3-carene oxide with sodium in benzene. The constants of the ketone purified by us through the semicarbazone are: b. p. 81-83°/7.5 mm, n^{20}_D 1.4705, d^{20}_4 0.9467, $[\alpha]_D = -110.6°$. The constants of L-3-carone are [2]: b. p. 98-99°/19 mm, n^{20}_D 1.4703, d^{20}_4 0.9507, $[\alpha]_D = -140°$. This same ketone was obtained by us in small yield by the dehydration of β-carene glycol with p-toluenesulfonyl chloride in pyridine, the study of which was undertaken several years ago with the aim of clarifying the course of the reaction (I or II).



In order to identify conclusively the described product of the hydrogenation of Δ^3-carene oxide over Raney Ni as L-3-carol, we prepared the latter by the action of sodium on Δ^3-carene oxide in benzene. Moreover, we also pursued another goal – the preparation of the product of the isomerization of the oxide by sodium, L-3-carone, and the study of its reduction by $LiAlH_4$.

From the alcohol fractions we prepared the 3,5-dinitrobenzoate of L-3-carol with a m. p. of 131-132° (from alcohol) and the acid phthalate with a m. p. of 158-159°, which showed no melting point depression in

mixed samples with the corresponding derivatives of the product of the hydrogenation of Δ^3-carene oxide over Raney Ni. Consequently, one of the products of the catalytic hydrogenation of Δ^3-carene oxide is L-3-carol.

Among the hydrogenation products, we also detected very small amounts of another $C_{10}H_{18}O$ alcohol, which gave a 3,5-dinitrobenzoate with a m. p. of 126-127° and a p-nitrobenzoate with a m. p. of 109-110°. From the melting point of the p-nitrobenzoate, the alcohol appears to be identical with the 4-carol formed by the action of sodium on Δ^3-carene oxide in benzene and first isolated by the Polish authors [2]. According to their data, 4-carol does not form an acid phthalate. We were also unable to prepare an acid phthalate.

It would appear that 4-carol could readily be isolated from the products of the catalytic hydrogenation of Δ^3-carene oxide by treatment with phthalic anhydride. However, this method was unsuccessful, probably because the alcohol is dehydrated by phthalic anhydride, a process which is indicated by the formation in this reaction of small amounts of phthalic acid. The crystalline products appeared to be a mixture of the derivatives of two alcohols. The following were isolated: the acid phthalate of L-3-carol with a m. p. of 158-159° (86%) and an acid phthalate with a m. p. of 102-103.5° and $[\alpha]_D = -38.96°$ (1.36% in benzene) (14%), which corresponded in analysis to the alcohol $C_{10}H_{18}O$. The latter could not be isolated in the pure form by saponification of the ester owing to the small amount of it.

The alcohol could be one of the four possible stereoisomers of 3-carol. It would naturally be expected that two of them would be formed during the reduction of L-3-carone by $LiAlH_4$, since according to [3, 4], under the influence of $LiAlH_4$ cyclic ketones give a mixture of stereoisomeric alcohols with a preponderance of the thermodynamically more stable isomers. The experiments showed that under these conditions, L-3-carone reacts to form a mixture of two stereoisomeric alcohols, the mixture consisting of 75% of the already known L-3-carol and 25% of an alcohol with the constants: b. p. 67.5-68°/3 mm, n^{20}_D 1.4826, d^{20}_4 0.9567, $[\alpha]_D = +43.57°$ (3.2% in ethanol); MR_{found} 45.93; $C_{10}H_{18}O$, MR_{calc} 46.20 including a contribution for the 3-membered ring. The alcohol gives a 3,5-dinitrobenzoate, m. p. 103-104°, and an acid phthalate, m. p. 114-115°, $[\alpha]_D = +40.46°$ (1.73% in benzene). Oxidation of the alcohol with chromium trioxide in acetic acid gave the original L-3-carone, m. p. of semicarbazone 201-202°.

In connection with the above, it seemed of interest to us to study the reduction of Δ^3-carene oxide with $LiAlH_4$.

According to the literature reports of preferential rupture of an oxide ring at the less substituted carbon atom [5-8], the reduction of Δ^3-carene oxide by $LiAlH_4$ would be expected to form the stereoisomeric tertiary alcohols as the main reaction products. We found the only reaction product to be 4-carol, described by the Polish authors [2], b. p. 76-77°/7 mm, m. p. 30-33°, $[\alpha]_D = +21.1°$ (2.8% in ethanol); yield 65.9%; m. p. of 3,5-dinitrobenzoate 126-127° (from gasoline, b. p. 66-70°), m. p. of p-nitrobenzoate 109-110°. Both esters melted without depressing the melting point when mixed with the corresponding derivatives of 4-carol isolated from the products of the catalytic hydrogenation of Δ^3-carene oxide.

LITERATURE CITED

[1] E. G. Isaeva and B. A. Arbuzov, Bull. Acad. Sci. USSR, Div. Chem. Sci. (In press).

[2] H. Kuczynski and L. Chabudzinski, Roczn. Chem. 29, 437 (1955).

[3] D. S. Noyce and D. B. Denney, J. Am. Chem. Soc. 72, 5743 (1950).

[4] J. B. Umland and M. J. Jefrain, J. Am. Chem. Soc. 78, 2788 (1956).

[5] J. D. Billimoria and N. F. Maclagan, J. Chem. Soc. (1951), 3067.

[6] M. Mousseron, R. Jacquier, M. Mousseron-Canet and R. Lagdoun, Compt. rend. 235, 177 (1952).

[7] M. Stoll and M. Hinder, Helv. Chim. Acta 34, 334 (1951).

[8] M. Vilkas, G. Dupont, and R. Dulou, Compt. rend. 242, 1329 (1956).

Received April 17, 1958

* See C. B. Translation.

ON THE INTERACTION OF INHIBITORS OF THE AUTOOXIDATION OF HYDROCARBONS WITH ALKYL AND PEROXIDE RADICALS

K. I. Ivanov and E. D. Vilianskaia

(Presented by Academician N. N. Semenov, December 27, 1957)

It has been previously shown experimentally that some inhibitors of the liquid-phase oxidation of hydrocarbons by molecular oxygen are able to retard the oxidation process only if they are added to the oxidizable material (white oil) prior to the beginning of the reaction, while others can inhibit when introduced at various stages of development of the process. It has been proposed that Group I inhibitors can tie up the active particles which initiate the chain reaction (chiefly hydrocarbon radicals, $R^{\cdot}$); Group II inhibitors interact with peroxide compounds which arise in the initiation stage (hydroperoxides, ROOH) and in the development stage of the reaction (ROOH and peroxide radicals $RO_2^{\cdot}$) giving inactive products [1]. This proposal has been confirmed by the absence of interaction of Group I inhibitors with hydrocarbon peroxides [2] and by their lack of effect on the thermal decomposition of hydroperoxides in solution, while Group II antioxidants sharply accelerate this process [1].

It was later found that there exists an inhibitor Group III which, like the representatives of Groups I and II, inhibits the autooxidation of hydrocarbons when added to the system prior to the beginning of the reaction, but which, in contrast to the inhibitors of Group II, is able to inhibit the developing (uninhibited) process only in its autocatalytic stage. A certain generality in the chemical structure of the inhibitors of each group was noted, and a classification of antioxidants on the basis of chemical criteria has been proposed [3].

With the aim of obtaining more complete experimental confirmation of the above-cited concepts of the nature of the action of antioxidants of Groups I and II and with the aim of elucidating the features of the action of the inhibitors of Group III, experiments were undertaken in which alkyl ($R^{\cdot}$) and peroxide ($RO_2^{\cdot}$) radicals were introduced directly into oxidizing white oil, and their effect on the activity of antioxidants of Groups I, II, and III in various stages of the oxidation of the oil was studied. The antioxidants used were p-hydroxydiphenylamine for Group I, 4,4'-diaminodiphenyl disulfide for Group II, and 2,6-di-tert-butyl-4-methylphenol (Ionol) for Group III; the first two were added in an amount of 0.1 mmole, and the third in an amount of 1 mmole per 100 g of oil. As the source of hydrocarbon radicals, $R^{\cdot}$, we used acetyl peroxide, which, as shown by Kharasch [4], decomposes in solution chiefly with the formation of CO_2 and CH_3 radicals according to the equation

Peroxide radicals, $RO_2^{\cdot}$, were obtained by the interaction of cumene hydroperoxide with Co naphthenate, which proceeds, according to Kharasch, in agreement with the scheme $C_6H_5C(CH_3)_2OOH + Co^{+++} \rightarrow C_6H_5C(CH_3)_2OO^{\cdot} + H^{+} + Co^{++}$. The acetyl peroxide was added (in the form of a 2% solution in petroleum ether) in an amount of 0.03 wt.% peroxide based on the oil, while the cumene hydroperoxide and the Co naphthenate were added in amounts of 0.3% and 0.01%, respectively. The raw white oil (ρ_4^{20} 0.8814) was purified [1, 3] immediately before an experiment. Oxidation of the oil (30 g) was carried out at 117° by bubbling oxygen through it in a glass apparatus, previously described [1], in the absence of metals. When the source of radicals was added before the start of the experiment, it was introduced into the oil before starting the oxygen flow, whence it was at the experiment temperature (in this case, the antioxidant was previously dissolved in the oil).

The results of the first series of experiments (Fig. 1) show that the introduction of $CH_3^{\bullet}$ radicals during the initiation stage of the reaction sharply accelerates oxidation of the uninhibited oil, practically eliminating the induction period of the process (curves 1 and 2, Fig. 1). The inhibitors of Groups I and III inhibit the start of the oxidation of the oil in the presence of added $CH_3^{\bullet}$ radicals, while the Group II inhibitors cannot do this (curves 4, Fig. 1). The latter also lose their stabilizing action when alkyl radicals are introduced before the start of the experiment, into oils inhibited by Group II inhibitors, while the inhibitors of Groups I and III completely protect the oil from oxidation under these conditions (curves 5, Fig. 1). When the antioxidants are added to oil which is being oxidized under the influence of added $CH_3^{\bullet}$ radicals (uninhibited oil), the inhibitors of Groups I and III, in contrast to the representatives of Group II, again completely arrest the process (curves 6, Fig. 1).

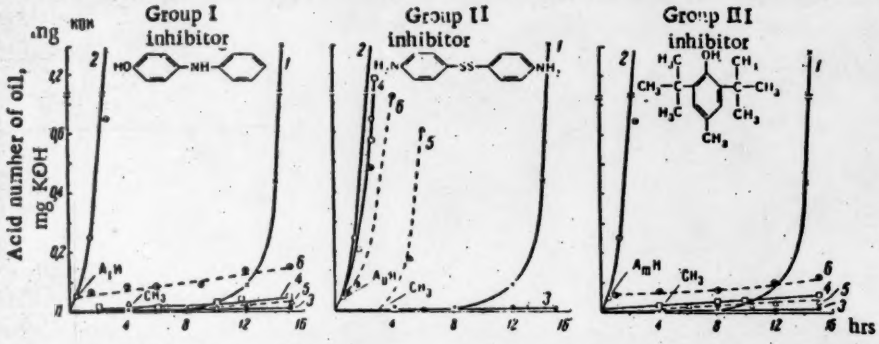


Fig. 1. The effect of the addition of a source of $CH_3^{\bullet}$ radicals on the oxidizability (increase in acid number) of uninhibited and inhibited white oil in various stages of the oxidation process. 1) Uninhibited oil; 2) inhibited oil containing a source of radicals added prior to the start of the experiment; 3) oil with antioxidant added prior to the start of the experiment; 4) oil containing an antioxidant and a source of radicals added prior to the start of the experiment; 5) inhibited oil after the addition of a source of radicals during the course of the experiment (time of addition is denoted by arrows); 6) uninhibited oil after the addition of antioxidant during the course of the experiment.

The same three antioxidants gave the same results under the same conditions when tetraethyllead was used as the source of radicals; the lead was added (in solution in oil) in an amount of 0.03%.

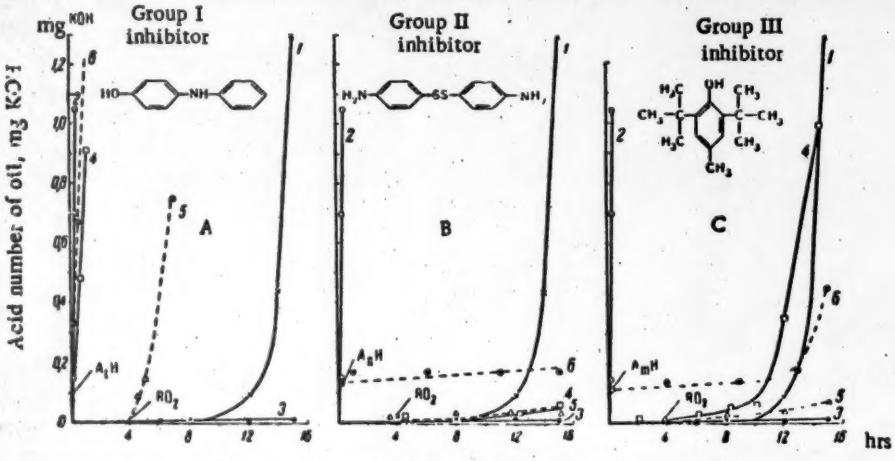


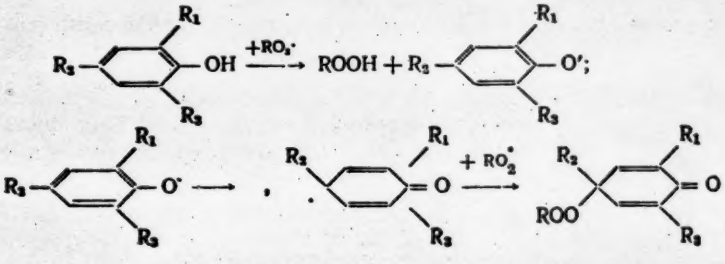
Fig. 2. The effect of the addition of a source of RO_2 radicals on the oxidizability of uninhibited and inhibited white oil in various stages of the oxidation process. Legends for the curves are the same as in Fig. 1.

The interaction, under analogous conditions, of these same antioxidants with peroxide radicals $C_6H_5 \cdot C(CH_3)_2OO\cdot$, was investigated in the second series of experiments. From the results obtained, which are presented in Fig. 2, it follows that the introduction of peroxide radicals in the initiation stage of the reaction also unusually strongly accelerates the oil oxidation process (control experiments showed that Co naphthenate and cumene hydroperoxide added separately cause less acceleration). The antioxidants of Groups II and III retain their inhibiting action when the $RO_2^\cdot$ radicals are introduced either before or after the beginning of oxidation (in the first case, Ionol, however, merely eliminates the accelerating effect of the introduced radicals) and also when these inhibitors are introduced into oil which is being oxidized under the influence of introduced radicals (Fig. 2, B and C). The antioxidant of Group I does not arrest the reaction when the $RO_2^\cdot$ radicals are introduced either before or after the beginning of the experiment. Its introduction into oil oxidizing under the influence of $RO_2^\cdot$ radicals also does not inhibit the reaction (Fig. 2, A).

Thus, the results of the test of the effect of $R^\cdot$ and $RO_2^\cdot$ radicals on the oxidation of inhibited oil show that inhibitors of Groups I and III retain their inhibiting effect in the presence of alkyl radicals, which confirms their ability to interact with these radicals at the instant that they appear, i.e., in the initiation stage of the chain reaction (with the formation of inactive radicals incapable of continuing the chain). Whence, it is readily visualized why the action of Group I inhibitors is limited to the period of reaction initiation. They are not in a condition to arrest the process in the development stage, since they react neither with $RO_2^\cdot$ radicals which propagate the chain (Fig. 2) nor with hydroperoxides [2] which are responsible for chain branching.

Assuming that the initiation stage of the oxidation process includes, in addition to the dissociation of molecules of the original hydrocarbon, RH, into free radicals (i.e., a reaction not requiring oxygen), also the direct reaction of the hydrocarbon with molecular O_2 [6a, 9] with the formation of the same free radicals directly or (more probably) with the intermediate formation of a peroxide compound ($RH \cdot O_2$ or ROOH, according to Bach), it may be supposed that Group II inhibitors inhibit the process in the initiation stage, interacting with these peroxides [2] with the formation of stable products, and they arrest already initiated and highly dispersed reaction owing to their ability, proved above, to react with $RO_2^\cdot$ peroxide radicals and also with hydroperoxides formed in this phase (secondary) of the reaction ROOH with the formation of stable products.

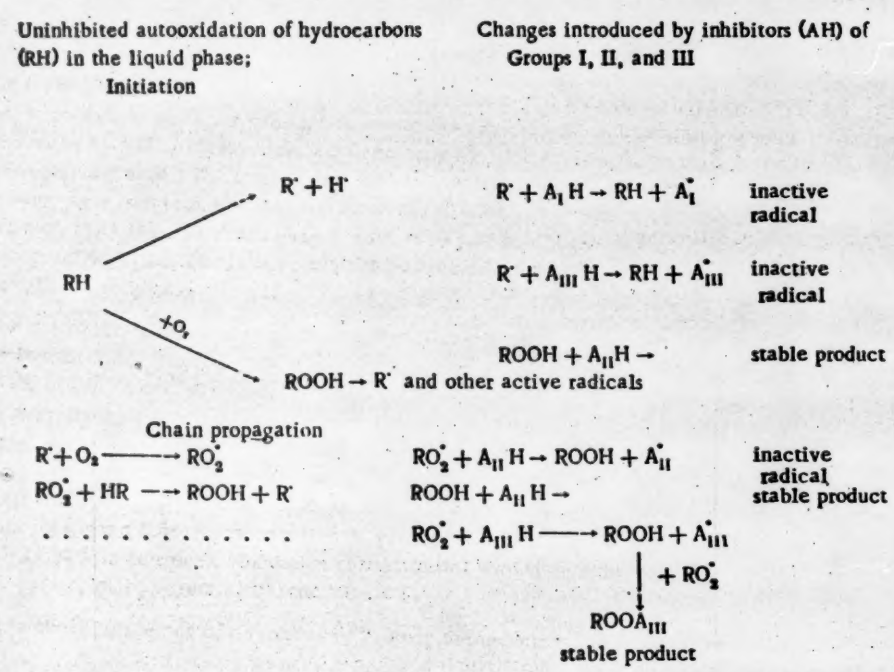
The mechanism of the inhibition of the oxidation process in the initiation stage by Group III inhibitors is the same as for Group I – the tying up of chain-initiating alkyl radicals. They inhibit the autooxidation stage of an initiated process by reacting with peroxide radicals, $RO_2^\cdot$. The chemical mechanism of this interaction, which has recently been elucidated for Ionol [7, 8], confirms the ability of one molecule of this inhibitor to combine with two peroxide radicals according to the scheme:



The loss of inhibiting action by Group III antioxidants when they are introduced into the system at a later stage of the reaction [3] is due to their inability (in contrast to Group II inhibitors) actively to react with hydroperoxides, which accumulate in this stage of the reaction and, decomposing partly by a chain mechanism, cause branching of the reaction chain [6b]. The results of the following experiments, carried out in our laboratory by V. K. Savinova and V. P. Zhakovskaia, confirm that Group III inhibitors react in the course of the oxidation process not with hydroperoxides, but with peroxide radicals. Cumene hydroperoxide (5 g) in solution in ethylbenzene (60 ml) was heated on an oil bath (170°): 1) in the pure form, 2) in the presence of Ionol (10 g), and 3) in the presence of Ionol (7 g) and Co naphthenate (0.2 g). In the first experiment, 86% of the hydroperoxide decomposed in 10.5 hours; in the second experiment, 70% decomposed in this same time, and 7.5 g of Ionol (m. p. 67°, identified by mixed melting point) was found in the residue; in the third experiment, 95% of the hydroperoxide decomposed in 3 hours. Ionol was not detected in the residue, and only 4 g of dimethylphenylcarbinol (m. p. 29°, identified by mixed melting point) and an unknown crystalline product with a m. p. of 180°

were found (a control experiment, carried out under these same conditions, showed that Ionol and Co naphthenate do not react in the absence of a hydroperoxide).

All of this experimental material permits the proposal that the initial stages of the process of hydrocarbon oxidation, inhibited by variously acting inhibitors, develop according to:


Uninhibited autooxidation of hydrocarbons (RH) in the liquid phase;
Initiation
Changes introduced by inhibitors (AH) of Groups I, II, and III
R· + H·
RH
+O₂
ROOH → R· and other active radicals
R· + A_I H → RH + A_I·
inactive radical
R· + A_III H → RH + A_III·
inactive radical
ROOH + A_II H →
stable product
Chain propagation
R· + O₂ → RO₂·
RO₂· + HR → ROOH + R·
RO₂· + A_II H → ROOH + A_II·
inactive radical
ROOH + A_II H →
stable product
RO₂· + A_III H → ROOH + A_III·
+ RO₂·
ROOA_III
stable product

LITERATURE CITED

[1] K. E. Ivanov and E. V. Vilianskaia, Coll.: Questions of Chemical Kinetics, Catalysis, and Reactivity,* Izd. AN SSSR (1955), p. 260.

[2] K. Ivanov and V. Savinova, ibid. (1955), p. 250.

[3] K. Ivanov and E. Vilianskaia, Chem. and Technol. of Fuels and Oils 4, 11 (1957).

[4] M. Kharasch et al., J. Org. Chem. 10, 386 (1945).

[5] M. Kharasch et al., J. Org. Chem. 17, 207 (1952).

[6] N. Semenov, a) On Certain Questions of Chemical Kinetics and Reactivity,* Izd. AN SSSR (1954), PP. 150, 242; b) J. Phys. Chem. 4, 4 (1933).

[7] T. Campbell and G. Coppinger, J. Am. Chem. Soc. 74, 1469 (1952).

[8] C. Boozer et al., J. Am. Chem. Soc. 77, 3233 (1955).

[9] B. Dolgoplosk et al., Coll.: Questions of Chemical Kinetics, Catalysis, and Reactivity, * Izd. AN SSSR (1955), p. 315.

All-Union F. E. Dzerzhinskii
Heat Engineering Scientific Research Institute

Received December 20, 1957

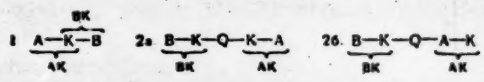
* In Russian.

ABSORPTION SPECTRA OF MOLECULAR COMPLEXES OF 9-(p-DIMETHYLAMINOSTYRYL)ACRIDINE WITH 10-ETHYL-9-(β-CARBOMETHOXYETHYL)ACRIDINIUM IODIDE

V. A. Izmail'skii and L. D. Vishnevskii

(Presented by Academician B. A. Kazansky, March 15, 1958)

It is universally accepted that a bathochromic color shift requires the presence of a continuous conjugated system, K, between the interacting chromophore components – the electrophilic (B) and electron-donor (A) components (endomolecular conjugation of chromophores, "optical conjugation" [1]). B and A together with K form a generalized π-electron system – a co-chromophore [1] (Scheme 1) [3].

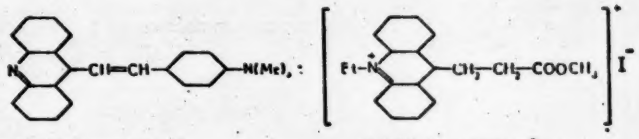


3 [AK + BK] or [AK⌒BK]*

* The arch conjugation symbol, ⌒, denotes a partial π-bond, in the present case an exo-ρ-bond [3].

Compounds with isolated chromophore systems AK and BK separated by a group which breaks the conjugation can also have a deep color [2, 3] when strong electron-donor (AK) and strong electrophilic (BK) groups are present (Schemes 2a or 2b). In this case, the deep color is associated with exomolecular conjugation, i.e., with direct interaction of the AK and BK systems through the external field between the molecules;* this occurs in the solid state in a crystal, in the melt, and also in concentrated solutions at concentrations of the order of 10^{-2} and higher. Hence, a third course arose in our investigations: the study of spectra of Type 3 donor-acceptor molecular complexes, i.e., complexes formed from strong electron-donor (AK) and strong electrophilic (BK) chromophore systems [3, 4]. We have systematically studied molecular complexes with a BK component containing the strong electrophilic immonium group $C = N^+$ using pyridinium and quinolinium salts [5, 6] and acridinium salts [7].

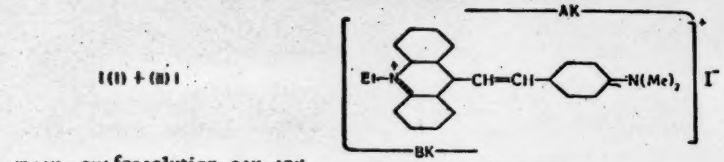
For the AK component we used 9-(p-dimethylaminostyryl)acridine (I), which contains $A = N(CH_3)_2$ and for the electrophilic BK component we used the ethiodide of 9-acridinepropionate (10-ethyl-9-(β-carbomethoxyethyl)acridinium iodide) (II). Substitution of the CH_3 group in the ethiodide of 9-methylacridine [7] by the group $CH_2CH_2COOCH_3$ was made with the aim of increasing the solubility.



I [AK] λ_{max} 434 mμ* II [BK] λ_{max} 406 mμ*

* Me denotes CH_3, Et denotes C_2H_5.

* In special cases, exointeraction through the external field in compounds of Type 2 can also occur within a molecule as a result of folding of the chain [3, 4].



III [AK⌒BK] for solution 3AK · 1BK λ_{max} 616 mμ IV B—K—A λ_{max} 616 mμ

At a molar ratio of components of 1AK:1BK and $c = 10^{-5}$, the color of the solution is pale yellow. The absorption curve indicates complete dissociation of the complex (Nos. 11 and 14, Fig. 1 and Table 1). However, already at $c = 2 \cdot 10^{-5}$ (No. 10), formation of a complex is observed in the appearance of a slight step around 570 mμ ($\epsilon_{max} \sim 75$). The band is already well formed at $c = 5 \cdot 10^{-5}$ (No. 9, Table 1 and Fig. 1, Nos. 9 and 10) (the color of the solution is yellow-green). With a further increase in the concentration to 10^{-4} and 10^{-3}, the color deepends to dark blue, and ϵ_{max} increases to 18,930 (Nos. 8 and 7, Table 1 and Fig. 1). This indicates a shift in the equilibrium to the side of the complex AK + BK ⇌ [AK BK] with respect to λ_{max}, calculated as the sum of the components (No. 14, Table 1 and Fig. 1), $\Delta\lambda = +161$ mμ. The equilibrium can be shifted to the side of the complex by using an excess of one component, 3AK:1BK or 1AK:3BK* (Nos. 12 and 13); λ_{max} goes to 616 mμ ($\Delta\lambda = 12$ mμ, ϵ_{max} is 30,340 (No. 13). It is of special interest to compare

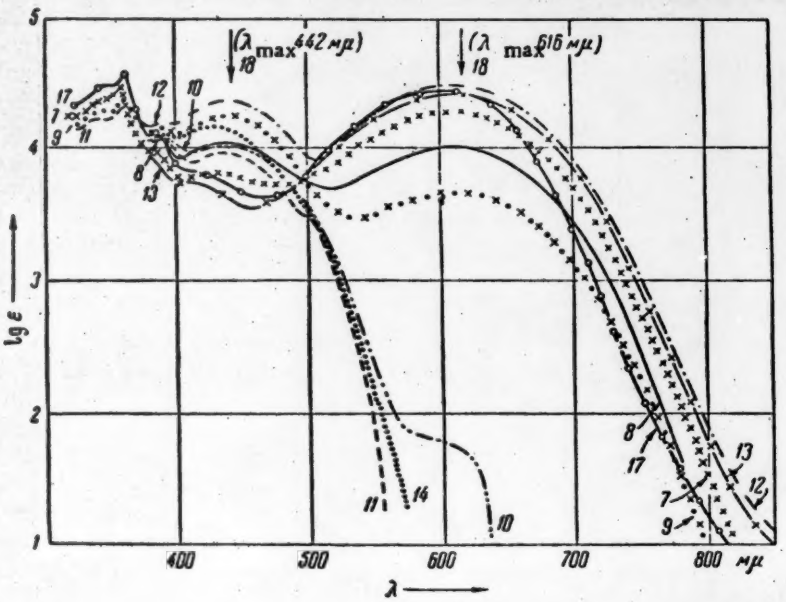


Fig. 1. Absorption spectra of molecular complexes between 9-(p-dimethylaminostyryl)acridine and 10-ethyl-9-(β-carbomethoxyethyl)acridinium iodide. Numbers on the curves correspond to the solution numbers in Table 1. Curve Nos. 8, 10, 12, 13, and 14 begin at 380 mμ owing to their superimposition on other curves.

the absorption spectra of molecular complexes of Type 3 acridinium compounds (III) with the spectra of the corresponding compounds with a Type 1 conjugated structure (IV). For solutions of the complex [AK + BK] (III) (Table 1, Nos. 12 and 13; Fig. 1) λ_{max} of 616 mμ agrees with λ_{max} of a dye with the conjugated system

* The differential method of spectroscopic recording was used [4, 6]. With an excess of one of the components (n moles:1), for comparison of the spectra a solution was used which contained n − 1 moles per liter of the component in excess.

B – K – A (IV) containing similarly constructed AK and BK systems superimposed one on the other. The similarity is so remarkable that the question arises as to whether λ_{max} of 616 mμ for the solution of the complex [AK + + BK] is not a consequence of alcoholysis of the acridinium salt with subsequent addition of HI to AK (see No. 19, Table 1). However, the following facts contradict this hypothesis:

TABLE 1 •

Comparison of the Absorption Spectra of AK (I) and BK (II) with the Spectra of the Molecular Complex [AK⁀BK] (III) and the Dye B – K – A (IV)

Solution No.	Structure	Ratio, molecular	c, mmole/liter	Absorption band of dye and complex			Absorption bands of components	
				λ_{max} mμ	ε_{max}	ε, % of № 12	λ_{max} mμ	ε_{max}
1	10-Ethyl-9-(β-carbomethoxyethyl)acridinium iodide	(I) BK	10^{-3}				406	3 930
							386	5 750
2	Same	(I) BK	10^{-4}				384	7 760
3	"	(I) BK	10^{-5}				384	9 800
4	9-(p-Me_2-N-styryl) acridine	(II) AK	10^{-3}				434	12 500
5	Same	(II) AK	10^{-4}				435	10 890
6	"	(II) AK	10^{-5}				436	9 960
7	[AK + BK]	1 AK : 1 BK	10^{-3}	605	18 930	62,4	430	6 240
8	Same	1 AK : 1 BK	10^{-4}	604	10 350	34,1	442	10 700
9	"	1 AK : 1 BK	$5 \cdot 10^{-5}$	604	4 660	15,3	436	17 120
10	"	1 AK : 1 BK	$2 \cdot 10^{-5}$	570	75	0,2	440	10 580
							387	12 750
11	"	1 AK : 1 BK	10^{-6}	none	0	0	440	8 910
							384	12 260
12	[AK + BK] AK in excess	3AK : 1BK	10^{-3}	616	30 340	100	438	22 380
13	[AK + BK] BK in excess	1 AK : 3BK	10^{-3}	616	25 970	85,6	412	5 750
14	[AK + BK] calculated	1 AK : 1 BK	10^{-3}				434	14 390
15	Same	1 AK : 1 BK	10^{-4}				435	11 250
16	"	1 AK : 1 BK	10^{-5}				436	10 000
17	[AK + BK] in chloroform	1 AK : 1 BK	10^{-3}	605	27 770	91,5	384	13 200
18	10-ethyl-9-(p-Me_2N-styryl) acridine	(IV)	10^{-3}	616			442	
19	9-(p-Me_2N-styryl) acridine in 0.01 N HCl	[AK·H]+Cl	10^{-3}	614	29 810	98,2	358	20 940

• Nos. 1-16, 18, and 19 in 96% ethanol; the absorption of Nos. 4, 5, 14, 15, 18, and 19 are from the data of V. A. Izmail'skii and S. V. Dmitrienko [7].

1. The linear dependence of the absorption coefficient on concentration in the region 604-616 mμ and the disappearance of absorption in this region on dilution to $c = 10^{-5}$ in Table 1 are presented as the values of ε_{max} in percent of that of solution No. 12, which was taken as 100 (Nos. 7-13).

2. The complete disappearance of color on the addition to the alcoholic solution of 2-3 drops of water (disintegration of the complex) was noted.

3. In chloroform,• where alcoholysis is impossible, there is more complete complex formation than in alcohol; the solution with $c = 10^{-3}$ has a deep blue color, and the band at 605 mμ is considerably more intense than it is in alcohol under the same conditions (Nos. 17 and 7). That the course of the curves Nos. 12, 13, and 7 differ somewhat from that of curve No. 17 in the 700-800 mμ region also shows that we do not have hydrolysis here and the formation of a salt with AK (I).

• Treated with soda, washed with water, dried over potassium carbonate, and distilled.

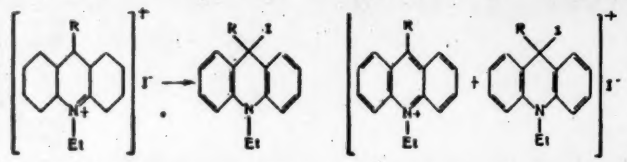
4. The intersection at one point of the spectral curves with a decrease in the concentrations from c = $= 5 \cdot 10^{-5}$ to 10^{-3} of solutions in alcohol (Nos. 7-10) and in chloroform (No. 17) indicates the presence of the equilibrium [AK + BK] ⇌ [AK ⌒ BK]. With an increase in ϵ_{max} in the 495-650 mμ region, ϵ_{max} in the 400-495 mμ region decreases.

5. The formation of colored complexes from quinolinium salts has also been observed with diphenylamine [3, 5, 9] and with p-aminoacetanilide [5].

The possibility of transesterification must also be discarded, considering that: 1) the solutions of AK and BK were prepared separately, and were not heated after mixing and before recording their spectra and 2) both components are acridinium compounds.

While complex formation was absent in the case of complex formation between 1-ethylquinolinium iodide and 4-(p-Me_2N-styryl)quinoline at a component ratio of 1:1 and $C = 10^{-3}$ [6], the formation of a complex from the acridine components (I) and (II) was observed at $c = 2 \cdot 10^{-5} - 5 \cdot 10^{-5}$ (Table 1, Fig. 1). The tendency toward complex formation is connected with the extension and area of the π-electron system of the planar molecule and increases in the order: pyridine derivatives [5] < quinoline derivatives [5] < acridine derivatives [7]. This can be considered as confirmation of the hypothesis that complex formation is absent as a result of lamellar association of planar molecules with the aid of partial electron bonds, exo-ρ-bonds, acting perpendicularly to the plane of the molecule along the axis of the π-electron cloud ("complex conjugation," "complex mesomerism") [2, 3, 5, 6, 10]. The remarkable similarity of the spectrum of the molecular complex (III) of the type [AK + BK] to the spectrum of the system B − K − A in dye (IV) is explained on the basis that the shift of the charge in the complex during excitation of the complex system by light proceeds along the π-electron system of the AK complex. Apparently, this is connected with the fact that the electron-donor system during complex formation acquired a partial (+) charge and that, as a consequence of the lamellar structure of the complex, the vector of the electron shift lies in the plane of the AK component (I).

In this connection and on the basis of [8] and investigations of molecular complexes of quinolinium [3, 5, 6] and acridinium [7] salts with components of the type AK, we advance the hypothesis that the bathochromic effect during an increase in the concentration of acridinium iodide (see 1-3, Table 1), especially for solutions in chloroform, is connected with the formation of the molecular complex (VII) of the type [AK' + BK]



V (BK) VI (AK') VII (BK + AK')

(BK is the acridinium salt (V), and AK' is its pseudosalt, Formula (VI)).

10-Ethyl-9-(β-carbomethoxyethyl)acridinium iodide (II). Brown needles from ethyl alcohol, m. p. 198-199°.

Found %: N 3.58, 3.60. $C_{19}H_{20}O_2NI$. Calculated %: N 3.33.

9-(p-Me_2N-styryl)acridine (I). M. p. 248° [7].

10-Ethyl-9-(p-dimethylaminostyryl)acridinium iodide. A blue substance (m. p. 310°, from alcohol [7]).

LITERATURE CITED

[1] V. A. Izmail'skii, Chem. Science and Industry 3, 233 (1958).

[2] V. A. Izmail'skii, Trans. 4 Conf. on Aniline-Dye Chemistry and Technology, October 14, 1939, Izd. AN SSSR (1940), p. 41; Proc. Acad. Sci. USSR 26, 906 (1940). *

[3] V. A. Izmail'skii, Trans. 8 Conf. on Aniline-Dye Chemistry and Technology, December 8-11, 1947, Izd. AN SSSR (1950), p. 87. *

* In Russian.

[4] V. A. Izmail'skii and A. N. Guseva, J. Gen. Chem. 24, 1402 (1954);* V. A. Izmail'skii, A. N. Guseva, and E. S. Solov'eva, J. Gen. Chem. 26, 1766 (1956).*

[5] V. A. Izmail'skii and P. A. Solodkov, Proc. Acad. Sci. USSR 60, 4, 587 (1948).

[6] V. A. Izmail'skii and P. A. Solodkov, Proc. Acad. Sci. USSR 75, 3, 391 (1950); 91, 5, 1119 (1953).

[7] S. V. Dmitrienko, Dissertation, (Moscow, 1958).**

[8] V. A. Izmail'skii, J. Russ. Chem. Soc. 52, 290, 303 (1920).

[9] A. F. Vompe, Proc. Acad. Sci. USSR 60, 5, 803 (1948). *

[10] V. A. Izmail'skii and D. K. Surkov, J. Gen. Chem. 13, 348, 834 (1943).

[11] H. Jenson and L. Howland, J. Am. Chem. Soc. 48, 1988 (1926).

[12] L. Volpi, Gaz. Chim. Ital. 22, 11, 552 (1892).

[13] C. Schenk, Ber. 39, 2425 (1906).

V. P. Potemkin Moscow Municipal
Pedagogical Institute

Received March 13, 1958

* Original Russian pagination. See C. B. Translation.
** In Russian.

A TRICLINIC MODIFICATION OF POLYTHENE

A. I. Kitaigorodskii and Iu. V. Mniukh

(Presented by Academician V. A. Kargin, March 1, 1958)

1. Paraffin-type molecules can crystallize in one of three modifications – triclinic (T), monoclinic (M), or rhombic (R) [1]. Two of these have been observed experimentally [2, 3]. Triclinic unit cells are found in normal paraffins with an even number of carbon atoms from C_{12} to C_{26} and in certain normal fatty acids; rhombic unit cells are found in polythene, n-paraffins with an odd number of carbon atoms or, from C_{28} up, with an even number, and in certain normal fatty acids, etc. A substance with a monoclinic unit cell has not been found; this is readily explained, since packing of this type is of low symmetry and less dense than both of the preceding.

The difference in free energy of R and T packings is small. This follows if only from the circumstance that several percent of neighboring homologs as impurities convert the triclinic structure of a n-paraffin to rhombic. The densest of all possible types of packing is that of the T unit cell; however, the R unit cell is more symmetrical. On the basis of an analysis of the packing of long-chain molecules, the probable existence of a triclinic modification of polythene was previously indicated [4].

2. Since the density of the molecular packing in a T unit cell is high, a T unit cell is feasible only in the most recent, from a structural point of view, polythene samples, i.e., the purest polythenes possessing a minimum amount of side branching. Therefore, the subjects of the present investigation were low-pressure polythene (presented by B. Kabanov), polythene prepared at a pressure of 100 atm. using tributylboron as a catalyst (presented by G. S. Kolesnikov and T. A. Soboleva), and polythene synthesized from diazomethane (presented by V. A. Sergeev).

X-ray powder patterns, obtained using CuK_α-radiation monochromatized by reflection from a crystal, showed that the investigated samples of polythene had a pattern characteristic of the two-phase system R + T. The triclinic modification was present in a smaller amount than the rhombic, as shown by a comparison of the intensities of the reflections. We had previously observed an analogous two-phase pattern during an investigation of the structural diagrams of n-paraffins [5].

TABLE 1

Interplanar Distances for the Most Intense Reflections

Modification	Interplanar distance, A				
$n\text{-}C_{20}$ T unit cell	4,54		3,79	3,58; 3,46	2,58
$n\text{-}C_{30}$ R unit cell		4,12 (110)	3,73 (200)		
Low pressure polythene (R + T)	4,55 (T)	4,12 (R)	3,71 (R)	3,47* (T)	2,58 (T)
Polythene from diazomethane (R+T)	4,55 (T)	4,14 (R)	3,72 (R)	3,53* (T)	2,58 (T)
$n\text{-}C_{30}$ under high pressure (R + T)	4,39 (T)	3,98 (R)	3,58 (R)		

Note. The interplanar distances marked with an asterisk are approximate owing to the closeness of the intense reflection (200) belonging to the R unit cell.

Both x-ray photographs are presented in Fig. 1 for comparison. Measurement of the interplanar distances and comparison of the intensities definitely confirmed the existence of a triclinic modification of polythene under ordinary conditions. The appropriate data are presented in Table 1.

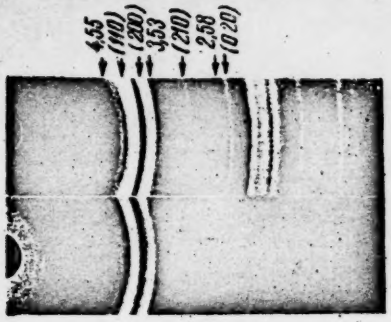


Fig. 1. A) One of the x-ray photographs of polythene containing both rhombic and triclinic modifications. (Lines of the R cell are indicated; for the T cell (marked on the photograph by arrows), the interplanar distances are indicated). B) X-ray photograph of 94% C_{18} + 6% C_{19} (presented for comparison). Two-phase region R + T.

A comparison of the x-ray photographs of the different samples of polythene shows that the reflections corresponding to the triclinic modification of polythene were relatively more intense in those cases where the crystal pattern possessed, on the whole, a higher degree of perfection (a large number of clear lines, the absence of amorphous dispersion).

Finally, we may compare our data with data from an x-ray investigation of C_{30} n-paraffin under high pressure (S. S. Kabalkina and L. F. Vereshchagin, private communication). The appearance of another phase along with the rhombic (see Table 1) was also observed for the n-C_{30} under high pressure. Since the crystal lattice is compressed under high pressure, the interplanar distances are decreased by 3%. Multiplying them by the appropriate factor, we obtain d_1 = = 4.55 A; d_2 = 4.12 A; and d_3 = 3.71 A. While both d_2 and d_3 both belong to an R unit cell, d_1 agrees with the interplanar distance of the strongest reflection of the triclinic modification of n-paraffins and polythene.

The nature of the packing in a triclinic unit cell of molecules of the type under consideration was established earlier by us [1, 6]. It can be assumed that the packing of triclinic polythene does not differ from the lateral packing of the molecular chains in triclinic n-paraffins.

Thus, the present work confirms the prediction of the existence of a triclinic modification of polythene, a prediction made by us previously.*

LITERATURE CITED

[1] A. I. Kitaigorodskii, Crystallography 2, 646 (1957).

[2] C. W. Bunn, Trans. Farad. Soc. 35, 482 (1939).

[3] A. Müller and K. Lonsdale, Acta Cryst. 1, 129 (1948).

[4] A. I. Kitaigorodskii, Crystallography 2, 456 (1957).

[5] A. I. Kitaigorodskii, Iu. V. Mniukh, and N. A. Nechitailo, Crystallography 3 (1958).

[6] A. I. Kitaigorodskii and Iu. V. Mniukh, Bull. Acad. Sci. USSR, Div. Chem. Sci. (1958), (In press).*

Institute of Heteroorganic Compounds
Academy of Sciences USSR

Received February 28, 1958

* While this article was still in press, we had an opportunity to become acquainted with the work of P. W. Teare and D. R. Holmes, J. Polymer Sci., 24, 496 (1957). These authors also experimentally observed the triclinic modification of polythene. The conclusion formed on the basis of the theory of packing of molecular chains has thus obtained new, independent proof.

* See C. B. Translation.

SYNTHESIS OF METHYLFERROCENE

A. N. Nesmeianov, E. G. Perevalova, L. S. Shilovtseva,

and Z. A. Beinoravichute

Recently, various mono- and dialkylferrocenes have been described; these were prepared by the direct alkylation of ferrocene in the presence of aluminum chloride [1-4] or by reduction of the corresponding ketones [5] and acids [6].

In the present work, we carried out the synthesis of methylferrocene by two routes: by reduction of the methyl ester of ferrocene carboxylic acid with lithium aluminum hydride (83% yield) and by reduction of the methiodide of N,N-dimethylaminomethylferrocene with sodium amalgam (94% yield). In the latter case, a small amount of the ether of ferrocenylcarbinol, $(C_5H_5FeC_5H_4CH_2)_2O$, was formed as a by-product.

EXPERIMENTAL

Preparation of methylferrocene from the methiodide of N,N-dimethylaminomethylferrocene.* A filtered solution of 1.2 g (0.0032 mole) of the methiodide of N,N-dimethylaminomethylferrocene [7, 8] in 60 ml of water was added to ice-water-cooled sodium amalgam prepared from 12 g of sodium and 12 ml of mercury. The reaction mixture was heated in an air bath at 90-100° for 8 hours. The resulting dark orange crystalline precipitate of methylferrocene was filtered and washed with water. The yield was 0.6 g (94% of theoretical). The methylferrocene was recrystallized from petroleum ether (the precipitate formed on cooling to − 10°), m. p. 35.5-36.5°.

Found %: C 66.26, 66.46; H 6.09, 6.11; Fe 27.80, 27.59. $C_{11}H_{12}Fe$. Calculated %: C 66.03; H 6.04; Fe 27.91.

The ether of ferrocenylcarbinol, $(C_5H_5FeC_5H_4CH_2)_2O$, along with some methylferrocene, was isolated chromatographically (over Al_2O_3) from the combined mother liquors from several experiments. The methylferrocene was eluted with petroleum ether, and the ether of ferrocenylcarbinol was eluted with ether or with a 1:4 mixture of ether and benzene. M. p. 128-129.5° (from petroleum ether).

Found %: C 64.21, 64.04; H 5.49, 5.45; Fe 26.92, 26.91. $C_{22}H_{22}OFe$. Calculated %: C 63.81; H 5.35; Fe 26.98.

Literature data [9]: m. p. 129-130°.

Though it decreased the yield of methylferrocene, a decrease in the excess of sodium amalgam permitted the reduction of a larger amount of the methiodide at one time.

Thus, 16 g of the methiodide of N,N-dimethylaminomethylferrocene was reduced by amalgam prepared from 46 g of sodium and 30 ml of mercury (heated for 12 hours). The methylferrocene was extracted with petroleum ether (twice with 80-100 ml). The methylferrocene, which crystallized after partial distillation of the solvent, had a m. p. of 33-34°. The yield was 6.1 g (75% of theoretical).

The residue remaining after extraction of the methylferrocene was dissolved in hot petroleum ether, methylferrocene (0.2 g), the ether of ferrocenylcarbinol (0.13 g), and ferrocenylcarbinol (0.15 g) were isolated chromatographically (over Al_2O_3) from the solution.

*Carried out jointly with Iu. A. Ustyniuk.

The amount of ether of ferrocenylcarbinol could be increased by adding the solution of methiodide to warm amalgam.

Preparation of methylferrocene from the methyl ester of ferrocenecarboxylic acid. To an ether solution of lithium aluminum hydride, prepared from 1 g of lithium hydride and 8 g of aluminum bromide, was added 1.75 g (0.072 mole) of the methyl ester of ferrocenecarboxylic acid. The reaction mixture was stirred vigorously for 4 hours while heating to boiling; it was then decomposed with water and dilute hydrochloric acid. The aqueous layer contained ionic iron. The ether solution was washed with soda solution and with water, and dried over magnesium sulfate. After distillation of the ether, the residue was dissolved in petroleum ether, and the methylferrocene was separated by chromatographic adsorption on aluminum oxide. The methylferrocene was readily eluted with petroleum ether. 1.2 g of methylferrocene was obtained. The yield was 83%. M. p. 35.5 to 36.5°. A mixture of this preparation with methylferrocene prepared from N,N-dimethylaminomethylferrocene melted without depression of the melting point (35.5-36.5°).

Found %: C 66.28, 66.42; H 6.20, 6.22; Fe 27.46, 27.31. $C_{11}H_{12}Fe$. Calculated %: C 66.03; H 6.04; Fe 27.91.

The infrared and ultraviolet spectra of the two methylferrocenes prepared by the different methods were identical.*

The i. r. spectrum (from vaseline oil): 810-820, 924, 1004, 1037, 1106, 1227, 1378, 1468, and 1655 cm^{-1}. The u. v. spectrum (in octane): λ_{max} (log ϵ_{max}): 324 (1.716) and 435 (1.921).

In another experiment, the reaction mixture described above was stirred for 1 hour at room temperature and for 3 hours while simmering. Ferrocenylcarbinol, in a yield of 77% of theoretical, and an 8% yield of its ether, identical with that obtained from N,N-dimethylaminomethylferrocene, were obtained.

Methylferrocene was prepared from ferrocenecarboxylic acid in a yield of 20% of theoretical (the reduction conditions were the same as for the methyl ester of the acid).

In work devoted to the alkylation of ferrocene under Friedel-Crafts reaction conditions, one of us and N. S. Kochetkov [2] described methylferrocene as having a m. p. of 118-119°. The methylferrocene prepared in the present work by the two routes described had a m. p. of 35.5-36.5°, and the data relating to this methylferrocene cannot be doubted. The reasons for this contradiction will be cleared up later.

LITERATURE CITED

[1] A. N. Nesmeianov and N. S. Kochetkov, Proc. Acad. Sci. USSR 109, 543 (1956). **

[2] A. N. Nesmeianov and N. S. Kochetkov, Proc. Acad. Sci. USSR 114, 800 (1957).**

[3] A. N. Nesmeianov and N. S. Kochetkov, Proc. Acad. Sci. USSR 117, 92 (1957).**

[4] M. Vogel, M. Rausch, and H. Rosenblum, J. Org. Chem. 22, 1016 (1957).

[5] A. N. Nesmeianov and N. A. Vol'kenau, Proc. Acad. Sci. USSR 107, 262 (1956).**

[6] A. N. Nesmeianov, E. G. Perevalova, and Z. A. Beinoravichute, Proc. Acad. Sci. USSR 112, 439 (1957).**

[7] C. R. Hauser and J. K. Lindsay, J. Org. Chem. 21, 382 (1956).

[8] J. K. Lindsay and C. R. Hauser, J. Org. Chem. 22, 355 (1957).

[9] P. G. Graham, R. V. Lindsey et al., J. Am. Chem. Soc. 79, 3416 (1957).

M. V. Lomonosov Moscow State University

Received March 12, 1958

* The spectra were obtained in the Laboratory of Molecular Spectroscopy of the Cathedra of Organic Chemistry, Moscow State University.

** Original Russian pagination. See C. B. Translation.

SYNTHESIS OF SILICON-CONTAINING VINYL ETHERS

Corresponding Member AN SSSR A. D. Petrov

and S. I. Sadykh-Zade

As is well known, polymers of vinyl ethers are raw materials for the production of lacquers, glues, synthetic leather, etc. [1]. The vinyl ethers themselves are obtained by a very simple reaction:

$$R-OH+HC\equiv CH\xrightarrow{KOH}R-OCH=CH_2, \qquad (1)$$

which is not, however, applicable to silanols, $\equiv Si-OH$ in view of the great ease with which both alkoxy- and alkenyloxysilanes decompose hydrolytically under the influence not only of electrophilic, but also of nucleophilic reagents.

It is possible to carry out vinylations according to Reaction (1) only in the case of such silicon-containing alcohols as γ-hydroxypropyltrimethylsilane [2], where, as a result of the considerable removal of the alcohol group from the silicon, the former has no effect on the silicon. We have also observed similar examples of the stabilization of molecules of organosilicon compounds with the removal of the functional group away from the silicon. Thus, for example, α-acetylenylsilane [3] could not be hydrated by Kucherov's method, while γ-butynylsilane, $\equiv Si-CH_2-CH_2C\equiv CH$ formed the corresponding ketone in good yield [4]. We should also note that in the case of silicoacetylenic (and silicoallenic) hydrocarbons – in complete analogy to acetylenic hydrocarbons – the triple bond shifts from the center to the end under the influence of heating with Na:

$$\equiv Si-C\equiv C-CH_3\xrightarrow{Na}\equiv Si-CH_2-C\equiv CH$$

$$\equiv Si-CH_2-CH=C=CH_2\xrightarrow{Na}\equiv Si-CH_2-CH_2-C\equiv CH.$$

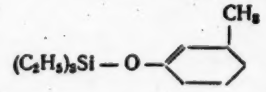
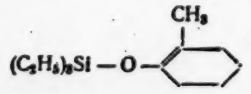
However, the reverse shift from the end to the center cannot be carried out with the silicon compounds, in contrast to acetylenic hydrocarbons, even in the case of γ-butynylsilane, owing to decomposition of the latter:

$$\equiv Si-CH_2-CH_2-C\equiv CH\xrightarrow[KOH]{H_2O}\equiv Si-O-Si\equiv+CH_3-CH_2-C\equiv CH.$$

In the present investigation, we were able to carry out, for the first time, the synthesis of vinyl ethers of the type $\equiv Si-O-CH=CH-R$, where R_1 is alkyl or aryl, only by means of a new reaction, specific to the chemistry of organosilicon compounds, in which trialkylsilanes are added to an α-β-unsaturated aldehyde or ketone in the presence of H_2PtCl_6. It was shown that the addition proceeds 1,4, the R_3Si adding to the carbonyl oxygen.

$$R_3SiH+\overset{1}{C}H_2=\overset{2}{C}H-\overset{3}{C}\overset{\overset{4}{O}}{\underset{H}{<}}\rightarrow CH_2-CH=CH-O-SiR_3, \qquad (2)$$

TABLE 1

Compound obtained	B. p. °C/mm Hg	n_D^{20}	d_4^{20}	MR_D found	MR_D calc.	Yield, % of theoretical	Found, % C	Found, % H	Found, % Si	Empirical formula	Calculated C	Calculated H	Calculated Si
β-Methylvinyloxytriethylsilane $(C_2H_5)_3Si-O-CH=CH-CH_3$	49—50/6	1,4320	0,8363	53,41	53,72	70,0	62,41	11,41	16,70	$C_9H_{20}SiO$	62,77	11,63	16,29
β-Benzylvinyloxytriethylsilane $(C_2H_5)_3SiO-CH=CH-CH_2-C_6H_5$	119—120/2	1,4960	0,9267	78,28	78,39	80	72,58	9,79	11,18	$C_{15}H_{24}SiO$	72,52	9,71	11,30
3-Methyl-1-cyclohexenyloxytriethylsilane 	82—83/2	1,4568	0,8823	65,54	65,48	90	67,95 68,13	11,58 11,40	12,95 13,53	$C_{12}H_{24}SiO$	67,93	11,32	13,21
2-Methyl-1-cyclohexenyloxytriethylsilane 	82—83/2	1,4550	0,8807	65,79	65,48	70				$C_{12}H_{24}SiO$	67,93	11,32	13,21

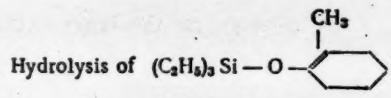
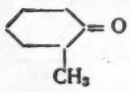
$$R_3SiH + CH_2=CH-\overset{\overset{O}{\|}}{C}-CH_3 \rightarrow CH_3-CH=\underset{\underset{CH_3}{|}}{C}-O-SiR_3 \qquad (3)$$

Addition according to Reaction (2) was carried out with acrylic and cinnamic aldehydes, while the addition according to Reaction (3) was to methyl vinyl ketone and to methylcyclohexanone. The silicon-containing ethers hydrolyze with the same ease as nonsilicon-containing vinyl ethers. They could be analyzed by forming oximes from the aldehydes (or ketones) resulting from their hydrolysis, hexaalkylsiloxanes being formed in place of alcohols, of course.

It was also possible to carry out the addition of $C_2H_5HSiCl_2$ to acrylaldehyde in the presence of this same catalyst.

$$CH_2=CH-\underset{H}{\overset{O}{C}} + \underset{\underset{H}{|}}{C_2H_5SiCl_2} \rightarrow (C_2H_5)Cl_2Si-O-CH=CH-CH_3. \qquad (4)$$

However, the resulting ethylmethylvinyloxydichlorosilane immediately polymerized to a thick liquid of the consistency of glycerin. On hydrolysis of this polymer, a solid, infusible polycondensation product was obtained, which was insoluble in ether and partially soluble in benzene. During an attempt to carry out Reaction (4) in pyridine, the entire contents of the flask was converted into a yellowish white mass. This product, which was homogeneous in appearance, was partially soluble in water. The floating, oil layer was rapidly converted into an amorphous, white product.

With the aim of obtaining proof of structure of the silicon-containing vinyl ethers, they were subjected to hydrolysis in the presence of traces of sulfuric acid with slight heating. For example, hydrolysis of $(C_2H_5)_3Si-O-CH=CH-CH_3$ gave propionaldehyde, b. p. 49-50°, which with 2,4-dinitrophenylhydrazine gave a hydrazone with a m. p. of 154-155°. Literature data [5]: m. p. 155°. Hydrolysis of  gave  2-methylcyclohexanone, the hydrazone of which had a m. p. of 136-137°. Literature data [5]: m. p. 136°.

It should be noted that the method developed by us for the synthesis of vinyl ethers is also a new method for the reduction of α,β-unsaturated aldehydes and ketones to the corresponding saturated compounds.

EXPERIMENTAL

β-Methylvinyloxytriethylsilane. In a liter flask fitted with a stirrer and a reflux condenser, which was protected by a calcium chloride tube, was placed 112 g of freshly distilled acrolein and 0.5 ml of a 0.1 N solution of chloroplatinic acid in isopropyl alcohol. The first 20 g of $(C_2H_5)_3SiH$ (of a calculated 174 g) was then added with continuous stirring. The temperature of the reaction mixture rose to 35° owing to exothermic heat. On subsequent heating on a water bath at 60°, the temperature inside the flask rose to 110°, as a result of which cooling had to be employed. The remaining $(C_2H_5)_3SiH$ was then added dropwise, the rate of addition being regulated so that the temperature did not exceed 45°. The reaction was completed by heating over the course of an hour to 120-140°. The unreacted acrolein and trialkylsilane were distilled at atmospheric pressure. The residue in the flask, 260 g, was distilled at 6 mm. A small amount of $(C_2H_5)_3Si-O-Si(C_2H_5)_3$, about 40 g of polymer (residue) and 160 g of β-methylvinyloxytriethylsilane were separated. A series of syntheses with other α,β-unsaturated aldehydes and ketones was carried out; the reactions went under analogous conditions, but without the evolution of heat. The properties of the resulting alkyl(aryl)vinyloxy- and cyclohexenyloxysilanes are presented in Table 1.

LITERATURE CITED

[1] I. Copenhaver and M. Bigelow, Acetylene and Carbon Monoxide Chemistry (New York, 1949) (First in a Collection on The Chemistry of Acetylene, Ed. by A. D. Petrov, (Foreign Lit. Press, 1954) (Translation).

[2] M. F. Shostakovskii and I. A. Shikhiev, Bull. Acad. Sci. USSR, Div. Chem. Sci. (1954), p. 745.*

[3] A. D. Petrov and S. I. Sadykh-zade, Proc. Acad. Sci. USSR, 86, 6, 1297 (1952).

[4] S. I. Sadykh-zade and A. D. Petrov, Proc. Acad. Sci. USSR 113, 3, 620 (1957).*

[5] W. C. Johnson, R. J. Shennan, and R. A. Reed, Organic Reagents for Organic Analysis, (Foreign Lit. Press, 1948), pp. 155-160 (Translation).

N. D. Zelinskii Institute of Organic Chemistry

Received February 6, 1958.

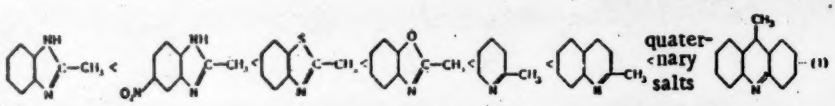
* Original Russian pagination. See C. B. Translation.

ISOTOPE EXCHANGE OF HYDROGEN AND THE REACTIVITY OF METHYL DERIVATIVES OF NITROGEN-CONTAINING HETEROCYCLES IN CONDENSATION REACTIONS

T. I. Abramovich, I. P. Gragerov, and V. V. Perekalin

(Presented by Academician A. N. Frumkin, March 18, 1958)

Nitrogen-containing heterocycles with a methyl group located in the α- or β-position with respect to the heteroatom, and their quaternary salts undergo condensation reactions with aldehydes, nitroso compounds, diazo compounds, nitroolefins [1] etc. These conversions usually proceed in an alkaline medium. On the basis of a large amount of qualitative data, the compounds under consideration can be arranged in the following series with respect to their activity:



The opinion is widely held (see, for example, [2]) that the rates of the condensation reactions and, indeed, whether or not they occur are determined by the ease with which protons are split from the methyl groups. In view of the fact that isotopic hydrogen exchange in an alkaline medium can serve as a direct quantitative characterization of the ease of proton removal, it appeared of interest to compare the rate of isotopic hydrogen exchange of these compounds with their tendency toward condensation reactions. Such an investigation is also important for clarification of the factors determining the dependence of the mobile hydrogen in a methyl group on structure.

In the present work, hydrogen exchange was studied between compounds of Series (I) and methyl alcohol-d, CH_3OD, in the presence of triethylamine. In the experiments with nitrogenous bases, the ratios of reagent, alcohol, and catalyst were approximately constant and equal to, respectively, 0.007 : 0.03 : 0.001 mole. The exchange in salts was studied in solutions 15-30 times more dilute. After exchange, isolation of the substances was carried out by vacuum distillation, in the case of the bases, and by crystallization from their solutions in CH_3OD by cooling, in the case of the salts. The refractions and melting points of the isolated substances corresponded to the literature values in all cases. The water obtained by combustion of these compounds was subjected to isotope analysis by the flotation method. The experimental data are presented in Fig. 1 in the form of graphs of $\ln(1-z)$ against the time t (z is the fraction exchanged calculated on the basis of three exchangeable hydrogen atoms in a methyl group).

The experimental points lie satisfactorily on the straight lines for a first order reaction. The average values of the rate constant K, presented in Table 1, were found from the slopes of these lines.

Under the conditions of our experiments, only the hydrogen of methyl groups located in α- or β-positions with respect to the heteroatom (not counting the hydrogen of the N–H bonds) underwent exchange. This conclusion is confirmed by the first order kinetics of the exchange, which indicates equivalence of all exchangeable atoms, by the observed cessation of the reaction after the exchange of 3H, and by the data of Shatenshtein and Zviagintseva [3, 4] on the exchange of α-picoline and of quinaldine with ND_3 and $C_2H_5OD + C_2H_5O^-$. As regards the hydrogen in methyl groups joined to the nitrogen in quaternary salts, it is well known that it does not

exchange under conditions much more severe than the conditions of our experiments [5]. Consequently, our order of exchange rates reflects the differences in the ease of proton removal from methyl groups.

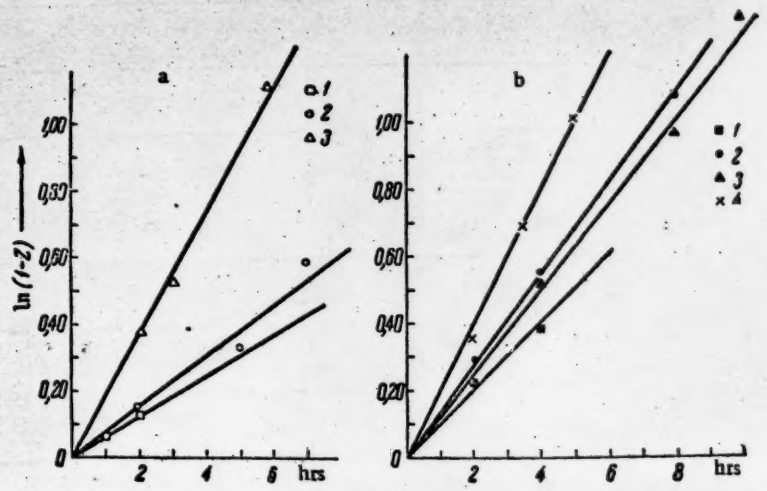
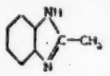
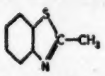
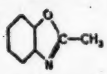
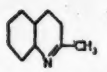
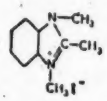
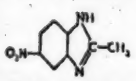
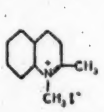


Fig. 1. Kinetics of exchange by methyl groups of nitrogen-containing heterocycles. a: 1) α-picoline, 180°; 2) 2-methylbenzthiazole, 180°; 3) 2-methylbenzoxazole, 180°; b: 1) 5-(6) nitro-2-methylbenzimidazole, 130°, 2) quinaldine, 150°, 3) 2-methylbenzimidazole, 130°, 4) 9-methylacridine, 70°.

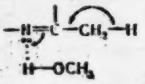
TABLE 1

Rates of Isotope Exchange of Hydrogen in Methyl Derivatives of Nitrogen-Containing Heterocycles

Substance	Exchange conditions, °C	Rate constant, $sec^{-1} \cdot 10^5$	Percent exchange	Substance	Exchange conditions, °C	Rate constant $sec^{-1} \cdot 10^5$	Percent exchange
	180	1,7			130	3,6	
	180	2,1			70	5,2	
	180	5,0			18 (8 min)		43
	150	3,8			18 (8 min)		72
	130	2,9			18 (8 min)		79

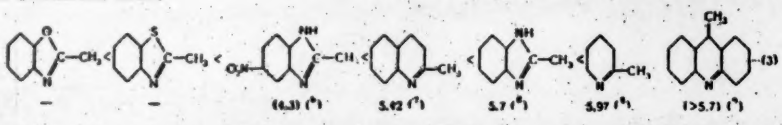
A comparison of Series (1) with the data of Table 1 shows that the activity in condensation reactions is not in conformity with the tendency toward proton removal from the methyl groups, and that, consequently, the ionization of hydrogen does not serve, at least in many cases, as the limiting stage in condensation reactions.

For an understanding of the dependence of the ease of isotope exchange on structure, it is important that the nitrogen of the compounds investigated form hydrogen bonds with the solvent in alcohol solutions. In such complexes:

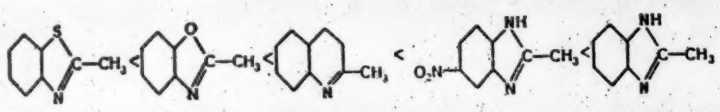


as was shown recently by Shatenshtein and Zviagintseva [3], ionization and exchange are considerably facilitated, since the electrophilic character of the nitrogen in these compounds is increased, which promotes the σ,π-conjugation represented in the scheme. It is obvious that the concentration of the complexes (2) is higher, the more basic the heterocycle.

However, the basicity order arranged on the basis of a direct knowledge of pK_A values (presented in parentheses) and chemical data:

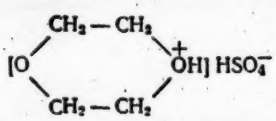


does not agree with the order of ease of exchange. Hence, it follows that conjugation of the type of (2) is not the sole cause of exchange. Apparently, another cause is conjugation with the aromatic rings in the ion $-N=C'-CH_2^-$, which increases the stability of this ion and, consequently, facilitates ionization. An increase in the number of rings and electrophilic substituents must contribute to such conjugation. These assumptions explain why 9-methylacridine exchanges more rapidly than quinaldine, and the latter more rapidly than α-picoline. Substances with an equal number of rings in the molecule can be arranged in the following series with respect to exchange rate:

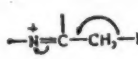


which agrees with Series (3) with the exception of the nitromethylbenzimidazole and the methylbenzoxazole, which is readily explained by conjugation with the nitro group and the inductive effect of the oxygen of the oxazole ring.

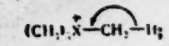
The excessive increase in exchange rate going on from the bases to the quaternary salts is very interesting. It is explained by the considerable increase in the σ,π-conjugation, similar to (2), which facilitates ionization. It is interesting that in this case the proximity of the aromatic ring facilitates ionization of hydrogen and exchange, as is seen on comparing the picoline salt with the salts of quinaldine and 2,3-dimethylbenzimidazole.

In the work of Kursanov, Setkina, and Bykova [5] with $[(CH_3)_4N^+]CH_3SO_4^-$, 

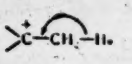
and other compounds it was shown that the inductive effect of N^+ or O^+ does not lead to significant labilization of the hydrogen in C—H bonds. We believe that only certain forms of conjugation can lead to such labilization: a) σ,π-form,

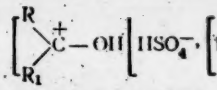
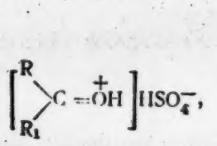
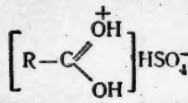
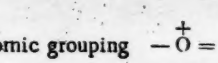
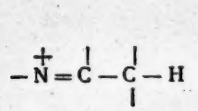


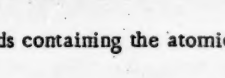
as was found in the present work; b) so-called σ,d-conjugation, consisting in a transfer of electrons from C—H bonds to vacant d-bands which causes rapid exchange in onium salts of phosphorus, sulfur, selenium, arsenic, etc.:



and, finally, c) similar conjugation which leads to exchange in carbonium ions [10]:



In the light of the data of this work, the exchange of hydrogen between concentrated acids and the α-positions in molecules of ketones and acids, which was observed by Kursanov and co-workers, should be explained not by the formation of carbonium salts,  and labilization of their hydrogen under the influence of C^+ [11], but by the emergence of onium compounds,  ,  , containing the atomic grouping  , analogous to the grouping  in the ammonium salts studied by us which also contained labilized hydrogen. Such a route has the advantage that an oxonium structure of these salts is considerably more probable than a carbonium structure.

It might be thought that compounds containing the atomic grouping  would more or less readily exchange their hydrogen for deuterium, especially in an alkaline medium. We propose to confirm this using amidine salts, salts of imido esters, and dimethylglyoxime complexes of metals, and also to determine whether it is possible for condensation reactions involving these substances to occur in alkaline media.

LITERATURE CITED

[1] V. V. Perekalin and A. S. Polianskaia, J. Gen. Chem. 27, 1933 (1957);* Proc. Acad. Sci. USSR 112, 441 (1957).*

[2] A. E. Porai-Koshits, Bull. Acad. Sci. USSR, Div. Chem. Sci. (1944), 39; Coll. Works (Moscow-Leningrad, 1949), p. 229.**

[3] A. I. Shatenshtein and E. N. Zviagintseva, Proc. Acad. Sci. USSR 117, 852 (1957).*

[4] A. I. Shatenshtein, J. Phys. Chem. 25, 1206 (1951).

[5] D. N. Kursanov, V. N. Setkina, and E. V. Bykova, Proc. Acad. Sci. USSR 97, 835 (1954); E. V. Bykova, Author's Abstract, Candidate Dissertation, Inst. Org. Chem., Acad. Sci. USSR (1953).**

[6] L. S. Efros and B. A. Porai-Koshits, J. Gen. Chem. 23, 697 (1953).*

[7] W. A. Felsing and B. S. Biggs, J. Am. Chem. Soc. 55, 3624 (1933).

* Original Russian pagination. See C. B. Translation.
** In Russian.

[8] H. C. Brown and X. R. Mihm, J. Am. Chem. Soc. 77, 1723 (1955).

[9] Heterocyclic Compounds, 4 (Moscow, 1955), p. 414.*

[10] W. V. Doering and K. Hoffmann, J. Am. Chem. Soc. 77, 521 (1955).

[11] D. N. Kursanov and V. N. Setkina, Proc. Acad. Sci. USSR 94, 69 (1954); V. N. Setkina and E. V. Bykova, Proc. Acad. Sci. USSR 92, 341 (1953); D. N. Kursanov and V. V. Voevodskii, Prog. Chem. 23, 642 (1954).

A. I. Gertsen Leningrad Pedagogical Institute
L. V. Pisarzhevskii Institute of Physical Chemistry
Academy of Sciences, USSR

Received March 17, 1958

* In Russian.

USE OF THE POLYCONDENSATION REACTION FOR THE PREPARATION OF POLYMERS

Corresponding Member AN SSSR V. V. Korshak,
S. L. Sosin, and M. V. Chistiakova

While carrying out free radical reactions in which the free radicals were generated by the decomposition of peroxides, many investigators have observed the formation of compounds which were dimers of radicals resulting from the removal of hydrogen from the solvent [1].

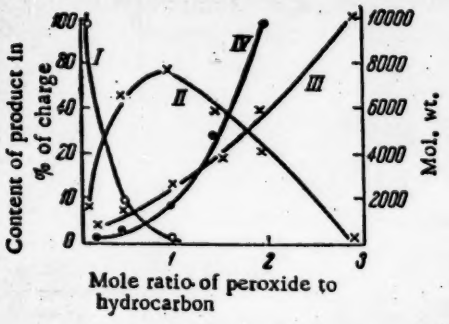


Fig. 1. Change in the composition of reaction products and molecular weight of the soluble polymer with changing ratio of peroxide to hydrocarbon. I) unchanged hydrocarbon; II) low-molecular-weight products; III) high-molecular-weight products (soluble and insoluble in benzene); IV) molecular weight of benzene-soluble polymer.

Our investigation showed that under specific conditions, the reaction can proceed in a manner such that the product will be not the dimer formed from the solvent, but high-molecular-weight compounds [2]. The formation of these compounds occurs as a result of a polyrecombination reaction. Subsequently, we obtained new experimental data, the presentation of which is the purpose of this article.

The basic data were obtained from reactions in which the starting material was diisopropyl benzene. Various peroxides served as the source of free radicals, major attention being given to tertiary butyl peroxide.

The reactions were carried out by gradually adding tertiary butyl peroxide, heated to a temperature of 170-200°, below the surface of the hydrocarbon. As a result, polymer was formed which, depending on the conditions under which the reaction was carried out, contained a greater or lesser amount of insoluble three-dimensional polymer. The soluble portion was separated by extraction with benzene and was dried with methanol. The resulting polymer was a white powder with a melting point of 210-230°.

X-ray investigation of this polymer showed that it was practically amorphous, since the degree of crystallinity did not exceed 10%. The insoluble polymer decomposed at a temperature above 300°, and, according to x-ray data, its crystallinity reached 60%.

We investigated the dependence of yield and molecular weight of the polymer formed on the amount of tertiary butyl peroxide. The results obtained are shown in Fig. 1; as seen from this figure, an increase in the molecular weight of the resulting polymer was observed as the amount of peroxide was increased. At a mole ratio of tertiary butyl peroxide to hydrocarbon of 1, practically all of the original hydrocarbon was converted into various reaction products. However, at this ratio, the amount of high-molecular-weight products was still small, and it continued to increase with an increase in the amount of peroxide until it reached 100% at a peroxide-to-hydrocarbon ratio of 3. Along with this, the amount of low-molecular-weight reaction products, comprising chiefly dimer and trimer, reached a maximum at a peroxide-to-hydrocarbon ratio of 1 and then decreased to zero at a ratio of 3. Thus, only the first mole of peroxide reacts with the original hydrocarbon.

The second and third moles react not with the original hydrocarbon, but with the products of the transformation, which, as we have already indicated, consists of a mixture of dimer and trimer.

The reaction which occurs with the formation of these polymers can be broken down into the following stages:

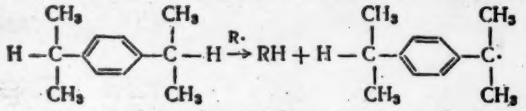
The first stage is the decomposition of the peroxide with the formation of free radicals:

$$(CH_3)_3COOC(CH_3)_3 \rightarrow 2(CH_3)_3C\dot{O} \rightarrow \dot{C}H_3 + (CH_3)_2CO.$$

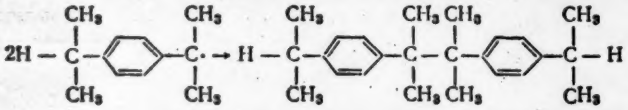
Both tertiary butoxy and methyl radicals are usually formed in a ratio depending on the temperature and properties of the solvent [3].

In an investigation of the kinetics of the decomposition of tertiary butyl peroxide in the liquid phase, Raley, Rust, and Vaughan [4] found that this decomposition is a monomolecular reaction, and were led to the conclusion that with an increase in temperature the stability of the butoxy radical decreases, and the reaction becomes more markedly one in which the butoxy radical decomposes with the formation of a methyl radical.

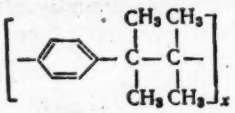
On the basis of the amount of tertiary butyl peroxide which we recovered, it can be concluded that about half of the peroxide taken decomposed with the formation of butoxy radicals. The free radical formed as a result of the decomposition of the peroxide acts on the p-diisopropylbenzene, extracting from it a tertiary hydrogen atom from an isopropyl group:



The resulting diisopropyl radical reacts with a similar radical forming the dimer according to the equation:



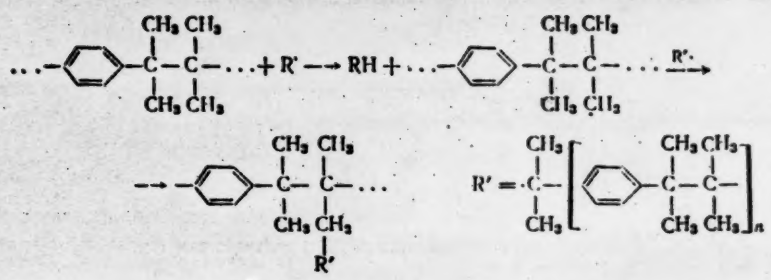
This dimer, in turn, can be subjected to the action of free radicals, and thus the growth of the polymer chain proceeds by stages leading to the formation of a polymer having the general formula:



Thus the polymer is formed as a result of numerous repeated acts of recombination of radicals arising from the solvent molecules. Therefore, we call this reaction a polyrecombination reaction.

As a method of synthesis of high-molecular-weight compounds, the polyrecombination reaction differs in principle from polymerization in that the primary products are saturated compounds, and, although the reaction proceeds by a radical mechanism, it has a stepwise, not a chain nature. The polyrecombination reaction has some characteristics which relate it to polycondensation reactions, among which are: the stepwise character of the increase in molecular weight and the presence of low-molecular-weight products – tertiary butyl alcohol and methane; however, in contrast to polycondensation reactions, it is an irreversible process, the reverse reaction of destruction of polymer chains [5] is not present.

The formation of insoluble, three-dimensional polymers apparently proceeds as a result of the interaction of radicals arising from the decomposition of the peroxide with hydrogen atoms of the methyl groups of the polymer.



As the reaction proceeds, the amount of tertiary hydrogen atoms continually decreases, and, therefore, interaction with methyl groups, which leads to branching of the polymer chain, becomes more probable. This is accompanied by the formation of an increasing amount of insoluble polymer, as may be seen from Fig. 2.

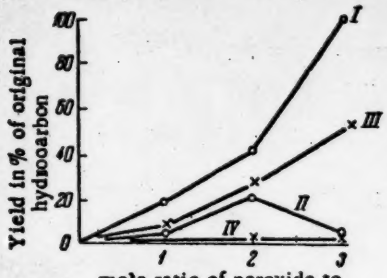


Fig. 2. Yield of benzene-soluble and insoluble polymers obtained in the presence of benzoic acid and without it. I) Insoluble polymer, without benzoic acid; II) soluble polymer, without benzoic acid; III) soluble polymer, benzoic acid present; IV) insoluble polymer, benzoic acid present.

We observed that with the use of benzoyl peroxide, even in larger amounts, no insoluble products were formed. This, obviously, can be connected with the benzoate radical which, being less active, does not react with hydrogen atoms of the methyl group.

We made use of this observation to decrease the amount of insoluble products; benzoic acid was added to the p-diisopropylbenzene, and only subsequently was the tertiary butyl peroxide added. It was found that with the addition of 0.5 mole of benzoic acid per mole of hydrocarbon, only soluble, linear polymer was formed, though with a lower molecular weight. The relationship between the linear and three-dimensional polymers obtained in the presence of benzoic acid and without it is shown in Fig. 2, from which it is seen that the presence of benzoic acid practically eliminated the formation of insoluble, three-dimensional products. Obviously, the benzoic acid is a modifier for the process and serves as a source of benzoate radicals, which leads to the formation of linear polymers only. The formation of benzoate radicals can be represented by the following equation:

$$C_6H_5COOH + (CH_3)_3CO\cdot \rightarrow C_6H_5COO\cdot + (CH_3)_3COH.$$

Some confirmation of such a mechanism is provided by the fact that when methyl benzoate is substituted for benzoic acid, insoluble polymer is again formed.

TABLE 1

Initial compound	Molecular wt. of polymer	M. p. of polymer, °C
Diphenyl	1500	136-166
p-Xylene	1600	108-130
Diisopropyl ketone	800	130-172
Diisopropylferrocene	8200	155-180
p-Dichlorobenzene	4500	230-280

We also carried out the preparation of polymers by means of the polyrecombination reaction starting with other substances. The results are presented in Table 1.

These results show that the polyrecombination reaction can be used with a wide range of starting materials as a method of synthesis of high-molecular-weight compounds.

LITERATURE CITED

[1] M. Kharasch, H. McBay, and W. Urry, J. Org. Chem. 10, 401 (1945).

[2] V. V. Korshak, S. L. Sosin, and M. V. Chistiakova, Bull. Acad. Sci. USSR, Div. Chem. Sci. (1957), 1271.*

[3] F. H. Dickey, J. H. Raley, et al., Ind. and Eng. Chem. 41, 1673 (1949).

[4] J. H. Raley, F. Rust, and W. Vaughan, J. Am. Chem. Soc. 70, 1336 (1948).

[5] V. V. Korshak, Prog. Chem. 21, 121 (1952).

Institute of Heteroorganic Compounds
Academy of Sciences, USSR

Received March 28, 1958

* Original Russian pagination. See C. B. Translation.

A NEW METHOD OF SYNTHESIS OF CYCLOBUTANE HYDROCARBONS

R. Ia. Levina, Iu. S. Shabarov, M. G. Kuz'min,

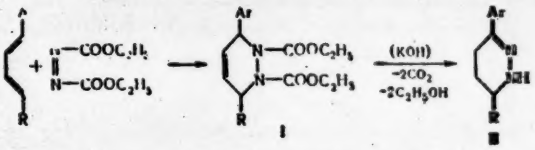
N. I. Vasil'ev, and E. G. Treshchova

(Presented by Academician A. N. Nesmeianov, February 27, 1958)

We recently made a brief preliminary report on the possibility of synthesizing hydrocarbons of the cyclobutane series by means of a new reaction – by the decomposition of tetrahydropyridazines.

In the present work, we studied several examples of this reaction.

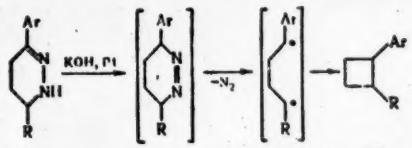
The initial tetrahydropyridazines (II) were readily obtained from the products (I) of the addition of diene hydrocarbons to the diethyl ester of azodicarboxylic acid by hydrolysis of these addition products, which proceeded with simultaneous decarboxylation and shifting of the double bond to the nitrogen [2]:



I

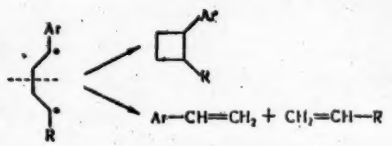
Ar=C_6H_5 (a+c), p-$CH_3C_6H_4$ (b); R=H (a+b) C_6H_5(c)

We were able to establish that tetrahydropyridazines, which are six-membered analogs of the pyrazolines, are decomposed by heating in the presence of potassium hydroxide and platinum with the evolution of nitrogen and the formation of cyclobutane hydrocarbons (in a manner similar to that by which pyrazolines form cyclopropanes in the Kishner reaction):



II III IV

It was shown that the intermediately formed biradical III not only cyclizes, but also breaks down with the formation of ethylenic hydrocarbons:



Analyses of the gases liberated during the decomposition of the initial monoaryltetrahydropyridazines (IIa and IIb) showed that the ratio of the amounts formed of arylcyclobutane and the corresponding styrene can be estimated from the ratio of the amounts of nitrogen and ethylene.

Thus, we are the first to extend the application of the classical Kishner reaction, which, up to the present, has been considered suitable only for the synthesis of cyclopropane hydrocarbons.

Phenylcyclobutane and two previously undescribed cyclobutanes, p-tolylcyclobutane and 1,2-diphenylcyclobutane, were synthesized by our reaction.

In one of our previous papers [3], it was shown that the intensities of the characteristic frequencies in the Raman spectrum of phenylcyclobutane are strong, approaching the intensities of these same frequencies for propenylbenzene (a hydrocarbon with a conjugated system of double bonds); this fact indicated the presence of conjugation between the benzene ring and the three-membered ring.

TABLE 1*

Propenylbenzene [3]	Phenylcyclopropane [3]	Phenylcyclobutane	Isopropylbenzene [4]	p-Tolylcyclobutane	p-Methylethylbenzene [4]
1208 (1065)	1220 (859)	1203 (600)	1212 (234)	1200 (1200)	1201 (560)
1304 (833)	1368 (600)	1300 (360)	1306 (90)	1368 (430)	1379 (220)
1600 (3256)	1607 (920)	1604 (690)	1606 (494)	1610 (1100)	1617 (585)

* The spectra were taken with an optical slit width of approximately 30 cm^{-1}. In the table, the integrated intensities calculated per mole of substance are given in parentheses.

A comparison of the intensities of some of the most intense frequencies (characteristic of the benzene ring) present in the Raman spectra of phenylcyclobutane with the intensities of the corresponding frequencies in the spectra of propenylbenzene and phenylcyclopropane, on the one hand, and with those of alkylbenzenes, on the other, showed that the monosubstituted aromatic hydrocarbons can be arranged in the following order: propenylbenzene > phenylcyclopropane > phenylcyclobutane > isopropylbenzene (see Table 1). The same frequencies in the spectrum of p-tolylcyclobutane have considerably higher intensities than in the spectrum of p-methylethylbenzene.

The increase in the intensities of the characteristic frequencies of the Raman spectra of phenylcyclobutane and p-tolylcyclobutane, as compared to these same frequencies for alkylbenzenes, indicates the presence of conjugation (though less clearly expressed than in the case of phenylcyclopropane) between the benzene ring and the four-membered ring.

EXPERIMENTAL

Preparation of the products of the addition of the diethyl ester of azodicarboxylic acid to 1-phenylbutadiene [5] (b. p. 75-77°/7 mm; n^{20}_D 1.6088) and with 1-p-tolylbutadiene (prepared by haloarylation of butadiene [6]; b. p. 95-97°/10 mm; n^{28}_D 1.5945, m. p. 26°; literature data [6]: b. p. 90-91°/9 mm, n^{28}_D 1.5970) was carried out by mixing solutions of equimolar amounts of the reagents in benzene while cooling (5-10° in the reaction mixture). The benzene was distilled, and the addition product was obtained by vacuum distillation.

3-Phenyl-1,2-dicarbethoxy-1,2,3,6-tetrahydropyridazine (90% yield): b. p. 169-171°/3.5 mm, m. p. 47° ((from aqueous methyl alcohol). Literature data [1]: b. p. 199-200°/7.5 mm, m. p. 47°.

3-p-Tolyl-1,2-dicarbethoxy-1,2,3,6-tetrahydropyridazine (90% yield; not described in the literature): b. p. 175-176°/2.5 mm, n^{20}_D 1.5195; d^{20}_4 1.1266; MR_D 85.85; calculated for $C_{17}H_{22}N_2O_4F_4$: MR_D 84.91; * ϵMR_D 0.94.

Found %: N 9.06, 8.86. $C_{17}H_{22}N_2O_4$. Calculated %: N 8.80.

The addition product of the diethyl ester of azodicarboxylic acid with 1,4-diphenyl-1,3-butadiene [8] (m. p. 152-153.5°) was prepared by heating equimolar amounts of the reagents (on a water bath) for two hours. The resulting 3,6-diphenyl-1,2-dicarbethoxy-1,2,3,6-tetrahydropyridazine (91% yield) melted at 132° (from ethyl acetate). Literature data [2]: m. p. 132°.

* The atomic refraction of nitrogen was taken as 2.48 [7].

Hydrolysis of the addition products of arylbutadienes with the diethyl ester of azodicarboxylic acid was carried out by refluxing for two hours on a water bath a solution of 0.25 mole of the addition product in 75 ml of ethyl alcohol with a solution of 70 g (1.25 mole) of potassium hydroxide in 300 ml of ethyl alcohol.

3-Phenyl-1,4,5,6-tetrahydropyridazine. At the conclusion of the reaction, the precipitated potassium carbonate was suction filtered and washed with ether. The solvent was distilled from the filtrate under vacuum, and the 3-phenyl-1,4,5,6-tetrahydropyridazine was separated by vacuum distillation. The yield was 79%. B. p. 179-181°/20 mm, m. p. 108° (from methyl alcohol). Literature data [1]: b. p. 160°/8 mm, m. p. 108°.

In order to isolate the 3-p-tolyl-1,4,5,6-tetrahydropyridazine and the 3,6-diphenyl-1,4,5,6-tetrahydropyridazine, the reaction mixture was poured into 600 ml of water, and concentrated hydrochloric acid was added to a neutral reaction. The precipitate was separated, washed several times with water, and purified by recrystallization.

3-p-Tolyl-1,4,5,6-tetrahydropyridazine (79% yield; not described in the literature): m. p. 49-52° (from petroleum ether); it oxidized slightly and deliquesced on brief standing.

3,6-Diphenyl-1,4,5,6-tetrahydropyridazine (82.5% yield): m. p. 159-160° (from ethyl acetate). Literature data [2]: m. p. 157-158°.

The decomposition of the tetrahydropyridazines was carried out by heating in a Wurtz flask a mixture of 0.1 mole of the tetrahydropyridazine with 0.2-0.3 g of potassium hydroxide and 0.05 g of platinum catalyst. A vigorous reaction began at about 250°, and partial distillation of the products occurred. In order to complete the reaction and the distillation of the resulting hydrocarbons, the temperature of the reaction mixture was raised to 250-300°. The distillate was washed with hydrochloric acid (1:1), a 2 N solution of soda, then with water, was dried with calcium chloride, and distilled in a column (except the diphenylcyclobutane) of 30 theoretical plates.

Phenylcyclobutane (from phenyltetrahydropyridazine). The yield was 35%; b. p. 105.6°/41.5 mm, 190°/750 mm; n^{20}_D 1.5269; d^{20}_4 0.9375; MR_D 43.32; calculated for $C_{10}H_{12}F_3\square$: MR_D 43.04. Literature data [9]: b. p. 190-191°/755 mm; n^{20}_D 1.5277, d^{20}_4 0.9378.

The second product of the reaction was styrene (43% yield): b. p. 63-64°/41.5 mm, n^{20}_D 1.5463; d^{20}_4 0.9075. Literature data [10]: b. p. 54°/30 mm; n^{20}_D 1.5450; d^{20}_4 0.9065. The gas evolved during the reaction consisted of nitrogen (65%) and ethylene (35%); the ethylene was identified as its dibromide (b. p. 130-131°, n^{20}_D 1.5370).

p-Tolylcyclobutane (from p-tolyltetrahydropyridazine). The yield was 42.5%, b. p. 93.5-93.7°/11 mm, n^{20}_D 1.5230; d^{20}_4 0.9275; MR_D 48.16; calculated for $C_{11}H_{14}\overline{=}_3\square$, MR_D 47.68.

Found %: C 90.29, 90.42; H 9.71, 9.71. $C_{11}H_{14}$. Calculated %: C 90.35; H 9.65.

Along with the p-tolylcyclobutane, p-methylstyrene (25.6% yield) was also formed during the decomposition of 3-p-tolyl-1,4,5,6-tetrahydropyridazine: b. p. 74.5°/29 mm, n^{20}_D 1.5397. Literature data [11]: b. p. 51°/10 mm, n^{24}_D 1.5395.

The gas evolved during the reaction consisted of nitrogen (73%) and ethylene (27%).

1,2-Diphenylcyclobutane (apparently a mixture of the cis- and trans- isomers; from diphenyltetrahydropyridazine). The yield was 7.2%, b. p. 154-155°/8 mm; n^{20}_D 1.5822; d^{20}_4 1.0305; MR_D 67.47; calculated for $C_{16}H_{16}\overline{=}_6\square$: MR_D 67.15.

Found %: C 92.40, 92.33; H 7.63, 7.67. $C_{16}H_{16}$. Calculated %: C 92.27; H 7.73.

The second product of the reaction, styrene, was obtained in a yield of 75%; b. p. 54-55°/30 mm, n^{20}_D 1.5446.

The Raman spectra (not described in the literature) of all of the arylcyclobutanes were taken with an ISP-51 three-prism spectrograph. The intensities of the lines in the spectra of phenylcyclobutane and p-tolylcyclobutane were measured photometrically and referred to a cyclohexane scale in which the integrated intensity of the 802 cm^{-1} line was taken as 500 units/mole. The intensities of the lines in the spectrum of 1,2-diphenylcyclobutane were evaluated visually in terms of an arbitrary scale in which the intensity of the 1603 cm^{-1} line was arbitrarily taken as 10 units.

Phenylcyclobutane: 257 (30), 316 (60; b), 354 (78, b), 406 (0), 55 (15), 620 (153), 645 (50), 735 (145), 769 (0), 792 (0), 809 (0), 842 (45), 877 (120), 907 (287; db), 950 (185, db), 996 (80), 1003 (960), 1036 (380) 1104 (120; b), 1154 (294), 1180 (334), 1203 (600; db), 1242 (30), 1300 (360; b), 1323 (178), 1354 (75), 1380 (20), 1443 (245), 1465 (20), 1545 (60), 1582 (65), 1604 (690).

p-Tolylcyclobutane: 218 (30/f), 257 (100; dif.), 322 (212; b), 370 (70; b), 420 (0), 547 (40), 590 (65; b), 621 (0), 645 (295), 718 (30/f), 738 (45), 792 (875), 809 (30), 875 (260), 908 (480; b), 949 (40), 996 (300), 1022 (0), 1085 (45), 1122 (45), 1151 (50), 1183 (440), 1200 (1200 db/f), 1219 (0), 1245 (45), 1270 (200), 1305 (60), 1342 (438; b), 1368 (430), 1443 (515), 1465 (50), 1566 (30;dif.), 1610 (1100).

1,2-Diphenylcyclobutane: 242 (1; b), 340 (0.5), 406 (0.5), 556 (0.5), 620 (3), 695 (0.5), 735 (1.5), 769 (0.8), 845 (0.5), 907 (1.5; db), 950 (1.5; db), 978 (1), 1002 (15), 1036 (4), 1085 (0.5), 1156 (2), 1183 (1), 1204 (5; b), 1296 (1; b), 1359 (1.5), 1443 (1.5), 1545 (1), 1571 (1), 1603 (10).

The intense lines at 620, 1003, 1036, 1203, and 1604 cm^{-1} in the spectra of phenylcyclobutane and 1,2-diphenylcyclobutane are characteristic of monosubstituted aromatics [4]; the 907-950 cm^{-1} lines are characteristic of a monosubstituted four-membered ring [12]. The most intense lines, characteristic of a disubstituted benzene [4], in the spectrum of p-tolylcyclobutane were: 645, 792, 996, 1204, and 1610 cm^{-1}; the cyclobutane ring was characterized by lines in the spectrum at 908, 925, and 949 cm^{-1}.

LITERATURE CITED

[1] R. Ia. Levina, M. G. Kuz'min, and Iu. S. Shabarov, Bull. Moscow State University, Chemistry, 1, 170 (1957).

[2] K. Alder and H. Niclas, Lieb. Ann. 585, 81 (1954).

[3] R. Ia. Levina, Iu. S. Shabarov, et al., Bull. Moscow State University, Chemistry 5 (1957).

[4] G. S. Landsberg, P. A. Bazhulin, and M. M. Syshchinskii, Basic Parameters of the Raman Spectra of Hydrocarbons,* Izd. AN SSSR (1956), p. 204.

[5] Organic Syntheses, Coll. 4 (Foreign Lit. Press, 1953), p. 504 (Translation).

[6] A. V. Dombrovskii and A. P. Terent'ev, J. Gen. Chem. 27, 2000 (1957).**

[7] V. R. Skvarchenko, M. G. Kuz'min, and R. Ia. Levina, Bull. Moscow State University, Chemistry 3, 169 (1957).

[8] Organic Syntheses, Coll. 2 (Foreign Lit. Press, 1949), p. 231 (Translation).

[9] F. Case, J. Am. Chem. Soc. 56, 715 (1934).

[10] H. B. Dykstra, J. Am. Chem. Soc. 56, 1625 (1934).

[11] P. B. Shorygin and N. V. Shorygina, J. Gen. Chem. 5, 555 (1935).

[12] V. G. Aleksanian, Kh. E. Sterin, M. Iu. Lukina, and L. A. Nakhapetian, Material from the 10th Conference on Spectroscopy,* 1 (1957), p. 68.

M. V. Lomonosov Moscow State University

Received February 26, 1958

* In Russian.

** Original Russian pagination. See C. B. Translation.

FLUORINE-CONTAINING ORGANOSILICON COMPOUNDS. FLUORINE-CONTAINING ORGANOSILICON ETHERS

Corresponding Member AN SSSR A. D. Petrov, V. A. Ponomarenko, and G. V. Odabashian

In preceding articles [1-3], we reported on the preparation of a number of fluorine-containing organosilicon compounds by the addition of silicon hydrides to fluoroolefins in the presence of platinized carbon, and on certain peculiarities of the reaction itself. In the present work, we transferred the study of the reaction of silicon hydrides with unsaturated compounds to ethers of allyl alcohol with 1,1,2-trifluoro-2-chloroethanol and with 1,1,2,2-tetrafluoroethanol,

$$CH_2=CHCH_2OCF_2CFClH \text{ (I) and } CH_2=CHCH_2OCF_2CF_2H$$

The aim of the present work was not only the preparation and study of the properties of previously undescribed fluorinated organosilicon ethers – we were also interested in the effect of the structures of the silicon hydrides and experimental conditions on the course of the addition reaction; for example, such substances as

$$Cl_3SiH,\ C_6H_5SiCl_2H,\ CH_3SiCl_2H,\ C_3H_7SiCl_2H,\ (C_2H_5)(CH_3)SiClH \text{ and } (C_2H_5)_2(CH_3)SiH,$$

i.e., compounds containing along with a Si–H bond a gradually decreasing number of chlorine atoms attached to the Si. The experiments were carried out under comparable conditions (heating for 3 hours at 170-180° in the presence of 0.3 g of 1% Pt on carbon in a 200 ml stainless steel autoclave). The results of the experiments and the reaction conditions are presented in Tables 1 and 2.

TABLE 1

$$\equiv Si-H+CH_2=CHCH_2OCF_2CFClH \rightarrow \equiv SiCH_2CH_2CH_2OCF_2CFClH$$

Original silicon hydride	Amt. g (moles)			Max temp. °C	Heating time hrs	Max. press., atm.	Reaction product	Yield	
	Orig. silicon hydride	I	1% Pt/C					g	%
Cl_3SiH	35.0 (0.26)	45.4 (0.26)	0.3	164	3	14	$Cl_3SiCH_2CH_2CH_2OCF_2CFClH$	30	38
$(CH_3)(Cl_2)SiH$	60 (0.52)	92.1 (0.53)	0.3	170	3	10	$(CH_3)(Cl_2)SiCH_2CH_2CH_2OCF_2CFClH$	115	76
$(C_2H_5)(Cl_2)SiH$	67.1 (0.52)	92.1 (0.53)	0.3	198	3	12	$(C_2H_5)(Cl_2)SiCH_2CH_2CH_2OCF_2CFClH$	121	76
$(C_6H_5)(Cl_2)SiH$	44.0 (0.3)	52.5 (0.3)	0.3	171	3	5	$(C_6H_5)(Cl_2)SiCH_2CH_2CH_2OCF_2CFClH$	59	61
$(CH_3)(C_6H_5)(Cl)SiH$*	33.0 (0.3)	52.5 (0.3)	0.3	182	3	15	$(CH_3)(C_6H_5)(Cl)SiCH_2CH_2CH_2OCF_2\times$ $\times CFClH$	43	50
$(CH_3)(C_6H_5)_2SiH$**	18.5 (0.18)	33.0 (0.19)	0.3	180	3	25	$(CH_3)(C_6H_5)_2SiCH_2CH_2CH_2OCF_2CFClH$	7	14
$(C_2H_5)(Cl_2)SiH$***	38.7 (0.3)	47.5 (0.3)	0.3	183	3	11	$(C_2H_5)(Cl_2)SiCH_2CH_2CH_2OCF_2CF_2H$	49	57

* $(C_2H_5)_2(Br)SiH$ also gave an 18% yield of an addition product with (I) (b. p. 124-125°/12 mm).
** $(C_2H_5)_3SiH$ added to (I) poorly under these conditions.
*** With ether (II).

As seen from Table 1, the following silicon hydrides gave the highest yields of addition products:

CH_3SiCl_2H, $C_2H_5SiCl_2H$, $(C_2H_5)(CH_3)SiClH$ and Cl_3SiH.

The increase in activity in this series of silicon hydrides is in agreement with our earlier observations [2] and also with the conclusions of Speier and co-workers [4] relative to the difference in the rates of addition of Cl_3SiH and CH_3SiCl_2H when chloroplatinic acid is used as the catalyst. The addition of CH_3SiCl_2H and of $C_2H_5SiCl_2H$ to (I), and also to other unsaturated compounds, in contrast to the remaining silicon hydrides, is accompanied by a sharp temperature rise. As the data of Table 2 indicate, the picture changed in experiments on the joint addition of a selected pair of silicon hydrides to (I). A comparison of the data of Tables 1 and 2 brings out the following:

TABLE 2

Original silicon hydride	Max. temp., °C	Max. pressure, atm	Distillation products	Amt. of dist. products, g	Yield of addition prods., % of theoretical
$C_2H_5SiCl_2H$	179	16	$C_2H_5SiCl_2H$	13.0	
Cl_3SiH*			Cl_3SiH	13.4	
			$(C_2H_5)(Cl_2)SiCH_2CH_2CH_2OCF_2CFClH$	38.6	52
			$Cl_2SiCH_2CH_2CH_2OCF_2CFClH$	38.7	52
$C_2H_5SiCl_2H$			$(C_2H_5)(Cl_2)SiCH_2CH_2CH_2OCF_2CFClH$	24.5	33
$(C_2H_5)(CH_3)SiClH$*	174	15	$(C_2H_5)(CH_3)(Cl)SiCH_2CH_2CH_2OCF_2CFClH$	28.7	33
			$C_2H_5SiCl_2H$		
$C_2H_5SiCl_2H$			$(C_2H_5)_2(CH_3)SiH$	22.0	
$(C_2H_5)_2(CH_3)SiH$**	189	15	$(C_2H_5)(Cl_2)SiCH_2CH_2CH_2OCF_2CFClH$	19.5	25
			$(C_2H_5)_2(CH_3)SiCH_2CH_2CH_2OCF_2CFClH$	33.0	47
Cl_3SiH			Cl_3SiH	20.0	
$(C_2H_5)_2(CH_3)SiH$*	159	9.5	$(C_2H_5)_2(CH_3)SiH$	9.3	
			$Cl_3SiCH_2CH_2CH_2OCF_2CFClH$	18.8	29
			$(C_2H_5)_2(CH_3)SiCH_2CH_2CH_2OCF_2CFClH$	27.5	33

* 0.3 mole of each silicon hydride and 0.3 mole of (I) were used in the reaction. The amount of catalyst (1% Pt/C) was 0.3 g. The reaction time was 3 hours.

** 0.25 mole of each silicon hydride and 0.25 mole of (I) were used in the reaction. The amount of catalyst and the reaction time were the same.

1. Our previous conclusion as to the high activity of silicon hydrides of the type of $RSiCl_2H$ and R_2SiClH is confirmed.

2. Trichlorosilane adds to (I) somewhat more difficultly than $C_2H_5SiCl_2H$ and $(C_2H_5)(CH_3)SiClH$. However, the addition of Cl_3SiH to (I) proceeds actively in the presence of $C_2H_5SiCl_2H$.

3. The addition of $(C_2H_5)_2CH_3SiH$ to (I) jointly with $C_2H_5SiCl_2H$ or Cl_3SiH proceeds with higher yields than in the absence of these chlorosilanes.

4. The data of Table 2 indicate that the alkylchlorosilanes studied can obviously be arranged in the following series with respect to activity in the addition reaction: $R_3SiH > R_2SiClH > RSiCl_2H \geq Cl_3SiH$. However, that the increase in the yield of the product of the addition of $(C_2H_5)_2(CH_3)SiH$ to (I) in the presence of Cl_3SiH or $C_2H_5SiCl_2H$, as in the case of trichlorosilane, is connected with "activation" of the reaction at the expense of the readily proceeding addition of $C_2H_5Cl_2H$ or Cl_3SiH to (I), cannot be excluded.

The majority of the fluorine-containing organosilicon ethers prepared, especially those containing a chlorosilyl group, are rather stable toward heating. The fluoro ether group of these compounds is not affected during Grignard reactions and hydrolysis.

EXPERIMENTAL

1,1,2-Trifluoro-2-chloroethyl ether of allyl alcohol $CH_2=CHCH_2OCF_2CFClH$ (I). This was prepared by a modification of the method described in [5]. In contrast to [5], we used a somewhat greater amount of

KOH and the reaction mixture was stirred. The $CF_2=CFCl$ was passed through a porous glass disc sealed at the bottom of the flask, which was fitted with a thermometer, a stirrer, and a reflux condenser. With this method, we were able to increase the yield of (I) from 45 to 89%. 400 g (6.89 moles) of allyl alcohol was used, and the reaction mixture was stirred in the presence of 70 g of KOH for 6 hours at a temperature not exceeding 25°; the product was washed with water, dried with Na_2SO_4, and distilled in a column with glass packing; this gave 1072 g (89%) of pure (I), m. p. 110°/755 mm. Literature data [5] 109.2°/750 mm.

1,1,2,2-Tetrafluoroethyl ether of allyl alcohol $CH_2=CHCH_2OCF_2CF_2H$ (II). This was prepared from allyl alcohol and tetrafluoroethylene under pressure; b. p. 74°/739 mm, d^{20}_4 1.2043; n^{20}_D 1.3273. MR found 26.58; MR calculated 26.70. The yield based on allyl alcohol was 80%.

1,1,2-Trifluoro-2-chloroethyl ether of γ-hydroxypropylmethyldichlorosilane $(CH_3)(Cl_2)SiCH_2CH_2CH_2OCF_2CFClH$ (III). 60 g (0.52 mole) of methyldichlorosilane and 92 g (0.53 mole) of (I) were heated for 3 hours at 170° in the presence of 0.3 g of 1% Pt on carbon. The maximum pressure was 10 atm. The weight of the reaction products was 147 g. Distillation in a column with glass packing gave 115 g (76%) of pure (III), b. p. 215°/753 mm, d^{20}_4 1.3395, n^{20}_D 1.4160. MR found 54.26; MR calculated 54.76.

Found %: C 25.33, 25.37; H 3.62, 3.61; Cl 36.49; F 19.68, 19.70. $C_6H_{10}SiCl_3F_3O$. Calculated %: C 24.89; H 3.48; Cl 36.72; F 19.68.

1,1,2-Trifluoro-2-chloroethyl ether of γ-hydroxypropylethyldichlorosilane $(C_2H_5)(Cl_2)SiCH_2CH_2CH_2OCF_2CF_2ClH$ (IV). The experimental conditions are shown in Table 1. The weight of the mixture of raw reaction products was 152 g. The (IV) had the following constants: b. p. 231.5°/751 mm, d^{20}_4 1.3155, n^{20}_D 1.4249. MR found 59.01; MR calculated 59.25.

Found %: C 27.93, 27.92; H 4.10, 4.04; Cl 33.50; F 18.01, 18.27. $C_7H_{12}SiCl_3F_3O$. Calculated %: C 27.69; H 3.99; Cl 35.00; F 18.77.

1,1,2-Trifluoro-2-chloroethyl ether of γ-hydroxypropyltrichlorosilane $Cl_3SiCH_2CH_2CH_2OCF_2CFClH$ (V). See Table 1 for the conditions of the experiment. The weight of the mixture of raw reaction products was 71 g. Distillation in a column with glass packing gave (V) with the following properties: b. p. 213°/753 mm, d^{20}_4 1.4563, n^{20}_D 1.4230. MR found 54.21; MR calculated 54.39.

Found %: C 19.92, 20.12; H 2.39, 2.48; Cl 46.91, 46.97; F 17.42, 17.13. $C_5H_7SiCl_4F_3O$. Calculated %: C 19.36; H 2.28; Cl 45.78; F 18.36.

1,1,2-Trifluoro-2-chloroethyl ether of γ-hydroxypropylpropyldichlorosilane $(C_3H_7)(Cl_2)SiCH_2CH_2CH_2OCF_2CFClH$ (VI). The experimental conditions are given in Table 1. The reaction products were distilled in a column and then under vacuum. The ether (VI), 59 g, had the following constants: b. p. 115.5°/8 mm, d^{20}_4 1.2763, n^{20}_D 1.4270. MR found 63.91; MR calculated 64.02.

1,1,2-Trifluoro-2-chloroethyl ether of γ-hydroxypropylmethylethyldichlorosilane $(CH_3)(C_2H_5)(Cl)SiCH_2CH_2CH_2OCF_2CFClH$ (VII). Under reaction conditions similar to those described above (see Table 1), 79 g of reaction products was obtained; distillation in a column gave (VII) with the following constants: b. p. 223°/746 mm, d^{20}_4 1.1918, n^{20}_D 1.4175. MR found 59.82; MR calculated 59.76.

1,1,2-Trifluoro-2-chloroethyl ether of γ-hydroxypropylmethyldiethylsilane $(CH_3)(C_2H_5)_2SiCH_2CH_2CH_2OCF_2CFClH$ (VIII). Distillation of 45.5 g of reaction products, which were obtained under conditions analogous to those described above (see Table 1), gave (VIII) with the following constants: b. p. 94°/7 mm, d^{20}_4 1.0776, n^{20}_D 1.4149. MR found 64.31; MR calculated 64.52.

Found %: C 43.37, 43.55; H 7.22, 7.49; Cl 13.70, 13.52; F 22.12, 21.81. $C_{10}H_{20}SiClF_3O$. Calculated %: C 43.38; H 7.29; Cl 12.81; F 20.59.

Original $(CH_3)(C_2H_5)_2SiH$ and (I) were isolated in amounts of 10 g and 14 g, respectively.

1,1,2,2-Tetrafluoroethyl ether of γ-hydroxypropylethyldichlorosilane $(C_2H_5)(Cl_2)SiCH_2CH_2CH_2OCF_2CF_2H$ (IX). The experimental conditions are presented in Table 1. From 80 g of reaction products, after distillation under vacuum, was obtained (IX): b. p. 207.2°/749 mm, d^{20}_4 1.2837, n^{20}_D 1.4033. MR found 54.63; MR calculated 54.46.

Found %: C 28.57, 28.51; H 4.22, 4.28; Cl 26.11, 25.95; F 26.99, 26.64. $C_7H_{12}SiCl_2F_4O$. Calculated %: C 29.27; H 4.21; Cl 24.70; F 26.47.

1,1,2-Trifluoro-2-chloroethyl ether of γ-hydroxypropyltrimethylsilane $(CH_3)_3SiCH_2CH_2CH_2OCF_2CFClH$ (X). This was obtained from 30 g of (IV) and CH_3MgBr prepared from 6.1 g of Mg and CH_3Br in 200 ml of absolute ether. After decomposition with water, the product was dried over Na_2CO_3 and distilled; 17 g (66% of theoretical) of (X) was obtained: b. p. 182°/742 mm, d^{20}_4 1.0866, $n^{20}D$ 1.3985. MR found 55.32; MR calculated 55.50.

Found %: C 39.25, 39.14; H 6.63, 6.58; Cl 14.90, 14.84; F 21.83, 21.99. $C_8H_{16}SiClF_3O$. Calculated %: C 38.63; H 6.48; Cl 14.25; F 22.92.

1,1,2-Trifluoro-2-chloroethyl ether of γ-hydroxypropyldimethylethylsilane $(CH_3)_2(C_2H_5)SiCH_2CH_2CH_2OCF_2CFClH$ (XI). This was obtained in an amount of 23.1 g (64%) under the conditions of the preceding experiment from 42 g of (V) and CH_3MgBr prepared from 12 g of Mg and CH_3Br in 300 ml of ether. The (XI) had the following constants: b. p. 204°/740 mm, d^{20}_4 1.0771, $n^{20}D$ 1.4073. MR found 60.09; MR calculated 60.01.

Found %: C 41.40, 41.63; H 7.01, 7.07; Cl 14.09, 14.13; F 22.29, 22.09. $C_9H_{18}SiClF_3O$. Calculated %: C 41.14; H 6.90; Cl 13.49; F 21.69.

The results of the experiments on the joint addition of silicon hydrides to (I) are presented in Table 2.

LITERATURE CITED

[1] V. A. Ponomarenko, B. A. Sokolov, and A. D. Petrov, Bull. Acad. Sci. USSR, Div. Chem. Sci. (1956), 628.*

[2] A. D. Petrov, V. A. Ponomarenko, B. A. Sokolov, and G. V. Odabashian, Bull. Acad. Sci. USSR, Div. Chem. Sci. (1957), 1206.*

[3] V. A. Ponomarenko, V. G. Cherkaev, A. D. Petrov, and N. A. Zadorozhnyi, Bull. Acad. Sci. USSR, Div. Chem. Sci. (1958), 247.*

[4] J. L. Speier, J. A. Webster, and G. H. Barnes, J. Am. Chem. Soc. 79, 974 (1957).

[5] J. T. Barr, K. E. Rapp, et al., J. Am. Chem. Soc. 72, 4480 (1950).

N. D. Zelinskii Institute of Organic Chemistry
Academy of Sciences USSR

Received January 29, 1958

* Original Russian pagination. See C. B. Translation.

SYNTHESIS OF THE METHYL ETHERS OF ISOMERIC CHONDROFOLINES, CHONDODENDRINES, AND TUBOCURARINES

V. G. Voronin, O. N. Tolkachev, and N. A. Preobrazhenskii

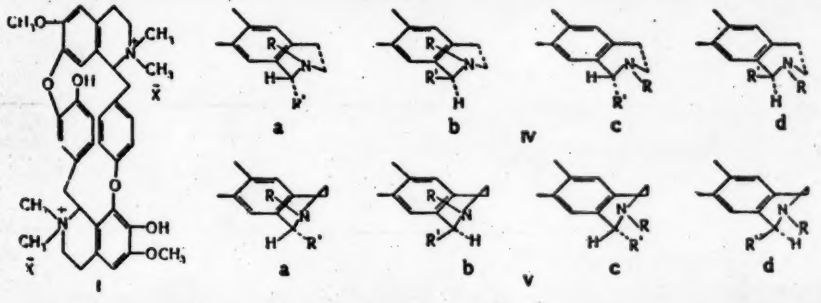
(Presented by Academician A. N. Nesmeianov, March 7, 1958)

Considering the D-tubocurarine (I) molecule [1], it can be seen that it has two asymmetric centers, which, according to classical structure theory, presumes the existence of two racemic forms and four optically active isomers.

Taking into consideration the basic aspects of conformation analysis, it is possible to write four racemic formulas for the tertiary base, chondodendrine (IIa, b, c, and d; R = H, R' = CH_3), and its quaternary salt, tubocurarine (IIIa, b, c, and d; R = H) only as a consequence of isomerism at C_1 and C_1'.

The formulas presented for the basic alkaloids of tube curare do not imply isomerism, which is dependent on the cis- and trans- positions of the substituents at the nitrogen of the tertiary bases and also on the conformations of the tetrahydroisoquinoline ring.

There is no information in the literature relative to the configurations of the tetrahydroisoquinolines. However, in conformity with recent work on tetralin and its derivatives, it can be assumed that tetrahydroisoquinoline rings can, in certain cases, exist in different forms: the chair form (IV a, b, c, and d) and the boat form (V a, b, c, and d), which are distorted as a consequence of the presence of the aromatic ring in the condensed system of the tetrahydroisoquinoline ring. These forms of isomerism apparently should occur also for the curare alkaloids, and correspondingly increase the number of possible isomers.



Moreover, in view of the nonplanarity in the structure of the macrocyclic diether system, which can be disposed in space in more than one way, the number of possible isomers is increased still further.

We have developed a scheme for the synthesis of chondrofoline, chondodendrine, tubocurarine, and their ethers which is distinguished by the appearance of the centers of asymmetry in the later stages of the synthesis; these later stages are carried out under mild conditions which do not lead to different types of isomerization, inversion, etc. By selecting appropriate conditions, we were able to carry out reactions with the formation of various isomers, and thereby to accomplish the synthesis of two isomeric O-methylchondrofolines (II, a-b, c-d; R = CH_3; R' = H), two isomeric O,O'-dimethylchondodendrines (II, a-b, c-d; R = R' = CH_3), and four isomeric O,O'-dimethyltubocurarine iodides (III a, b, c, and d; R = CH_3; X = I).

The syntheses were carried out as follows:

Previously prepared 1-(4'-hydroxybenzyl)-6-methoxy-7-[2"-methoxy-5"-(6"', 7"'-dimethoxy-8"'-bromo-3"', 4"'-dihydroisoquinolyl-1"'-methyl)-phenoxy]-3,4-dihydroisoquinoline [1] (VI) was subjected to Ullmann condensation in the presence of copper, potassium carbonate, and pyridine, and the product, without isolation, was reduced with zinc and dilute acetic acid. From the products of this reaction, the hydrochlorides of two isomeric forms of O-methylchondrofoline (II, R = CH_3, R' = H) were separated: A, m. p. 120-125° and B, m. p. 181-185°.

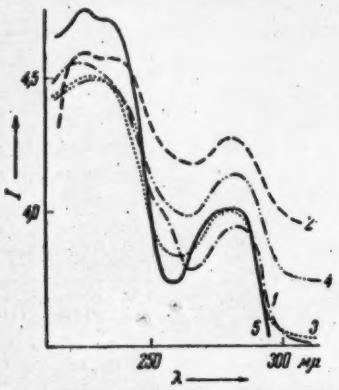


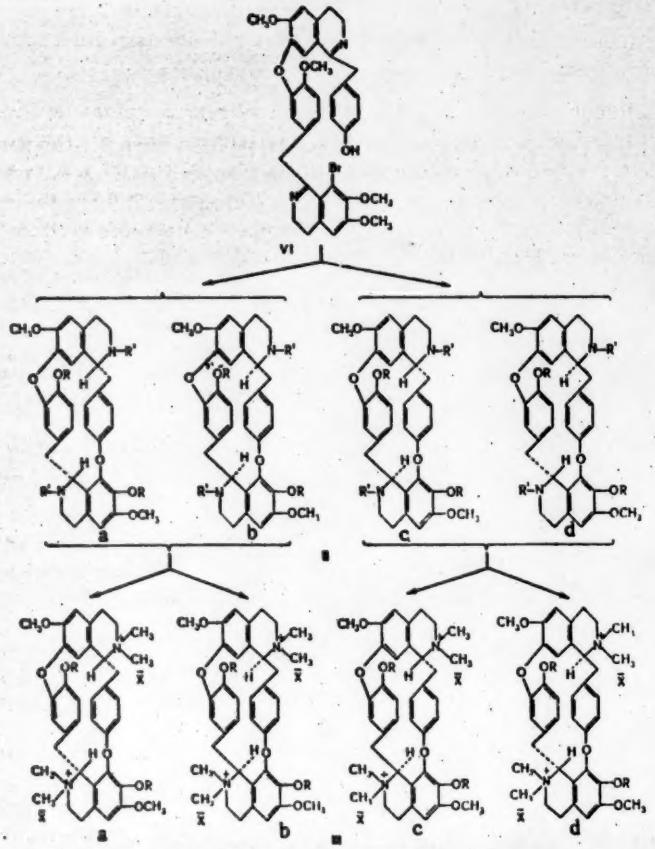
Fig. 1. Ultraviolet spectra of the dimethyl ethers of tubocurarine iodide. 1-4) Number of the salt (corresponding to the numbers in the text); 5) natural ether.

It should be noted that this reaction proceeds with high yield when substances with exposed phenolic hydroxyls are used, i.e., in the synthesis of chondrofoline and tubocurarine.

The bases II (R = CH_3, R' = H), A and B, were converted by the action of methyliodide into the hydriodides of the corresponding isomeric O,O-dimethylchondodendrines (II) (R = R' = CH_3): A, m. p. 159-163° (from ethyl alcohol) and B, m. p. 173-176.5° (from ethyl alcohol).

From the latter, the iodides of four quaternary ammonium bases III (R = CH_3, a, b, c, and d) were prepared.

Salts were prepared from base II (R = CH_3, R' = H), A (see Fig. 1).



1. M. p. 198-201° (from water). λ_{max} (alcohol) 230, 280 mμ (log ε 4.5752; 3.9403); λ_{min} 265 mμ (log ε 3.7795).

Found %: C 49.6, 49.97; H 5.11, 4.95; N 2.71, 2.72. $C_{40}H_{48}O_6N_2I_2 \cdot 3H_2O$. Calculated %: C 50.0; H 5.59; N 2.92.

2. M. p. 137-139° (from an ethyl alcohol–ether mixture). λ_{max} (alcohol) 225, 280 mμ (log ε 4.5996, 4.2748); λ_{min} 265 mμ (log ε 4.1763

Found %: C 50.22, 50.10; H 5.33, 5.38; N 2.81. $C_{40}H_{48}O_6N_2I_2 \cdot 3H_2O$. Calculated %: C 50.0; H 5.59; N 2.92.

The following salts were prepared from base II (R = CH_3, R' = H), B:

3. M. p. 257.5-259° (from ethyl alcohol). λ_{max} (alcohol) 225, 280 mμ (log ε 4.5090, 4.0426); λ_{min} 260 mμ (log ε 3.8353).

Found %: C 49.5, 49.85; H 5.41, 5.1; N 3.07, 2.90. $C_{40}H_{48}O_6N_2I_2 \cdot 3H_2O$. Calculated %: C 50.0; H 5.59; N 2.92.

4. M. p. 195-197° (from acetone–ether mixture). λ_{max} (alcohol) 225, 280 mμ (log ε 4.4920, 4.1323); λ_{min} 260 mμ (log ε 3.9780).

Found %: C 53.16; H 5.2; N 3.00. $C_{40}H_{48}O_6N_2I_2$. Calculated %: C 52.9; H 5.29; N 3.09.

The third sample corresponded most closely to the natural dimethyl ether of tubocurarine iodide.

M. p. 262-264° (from ethyl alcohol). λ_{max} (alcohol) 225,280 mμ (log ε 4.7585, 4.0735); λ_{min} 260 mμ (log ε 3.7308).

Found %: C 49.9; H 4.56. $C_{40}H_{48}O_6N_2I_2 \cdot 3H_2O$. Calculated %: C 50.0; H 5.59.

LITERATURE CITED

[1] L. V. Volkova, O. N. Tolkachev, and N. A. Preobrazhenskii, Proc. Acad. Sci. USSR 102, 3, 521 (1955).

M. V. Lomonosov Moscow Institute of
Fine Chemical Technology

Received March 7, 1958

ON CERTAIN REGULARITIES OF MELTING POINT CHANGES IN HOMOLOGOUS SERIES OF HETEROCHAIN POLYMERS

Corresponding Member AN SSSR V. V. Korshak and T. M. Frunze

The question of the connection between the structure of polymers and their properties is of great interest and has been the object of numerous investigations.

We have previously pointed out the presence of a connection between melting point and the structure of the polymer chain in a series of heterochain polyamides with an even number of methylene groups per unit [1]. This relationship between melting point and the ratio of amide and methylene groups is given by the equation $y = 7x + 110$, where y is the melting point and x is the ratio of amide to methylene groups in mole percent. The presence of a graphic relationship between melting point and the number of atoms in a unit of polyamides has also been noted by Champetier and Aelion [2] and by Hill and Walker [3].

A more careful consideration of this question, subsequently carried out by us, showed that the linear relationship applies not only in the series of even polyamides, but also in other series of heterochain polymers. For this purpose, we considered homologous series of polyureas, polyamides, polyurethans, polyesters, and polyanhydrides. It was shown that in all of these series there exists a quite specific relationship between the number of methylene groups per unit and the melting points of the polymers. We treated the material on polyamides in some detail [4]; the remaining classes of compounds were touched upon more sketchily just in order to show that the questions under consideration have general significance for all classes of heterochain polymers.

The similarity among the above-indicated different types of polymers proved to be sufficiently close that when the relationship between melting point and the heterochain characteristic (the heterochain characteristic is the ratio of the number of heterobonds per unit to the number of methylene groups, the ratio being expressed in percent [5]) was represented graphically, all of the lines of the graph intersected the ordinate axis in a single point.

As seen from Fig. 1, a , the experimental points in each series are well represented by straight lines. Thus, in each series of identically constructed polyamides, as in other classes of compounds which we will consider below, there is a linear relationship between melting point and heterochain characteristic. The slope of the lines expressing the relationship between melting point and heterochain characteristic varies in a manner which is dependent on the structure of the unit. In the polyamide series, the greatest slope belongs to polyamides obtained from acids and diamines with an even number of methylene groups in the molecule. It is interesting to note that the slope is sensitive to whether there is an odd number of methylene groups in the diamine or in the dicarboxylic acid. In the case where we have a dicarboxylic acid with an even number of methylene groups and a diamine with an odd number, the slope of the corresponding line is greater than in the case where we have a polyamide obtained from dicarboxylic acids with an odd number of methylene groups and diamines with an even number of methylene groups in the molecule. Lines corresponding to polyamides obtained from dicarboxylic acids and diamines with odd numbers of methylene groups in the molecule have the least slope.

The data obtained for polyurethans, polyureas, and polyanhydrides are presented in Fig. 1, b. Here we also observe a linear relationship between melting points in homologous series of the indicated polymers and the values of their heterochain characteristics, the slope of the lines changing sharply on going from polyureas to polyurethans to polyanhydrides; while for the first two classes of compounds an increase in melting point with an increase in heterochain characteristic is observed, the polyamides present the reverse picture – the melting point decreases with an increase in heterochain characteristic.

A similar relationship is also observed in the case of the polyesters, as may be seen from the graph presented in Fig. 1, c, and in the case of the polyesters there is also a difference between polyesters from dicarboxylic acids with an even number of methylene groups and polyesters obtained from acids with an odd number of methylene groups in the molecule.

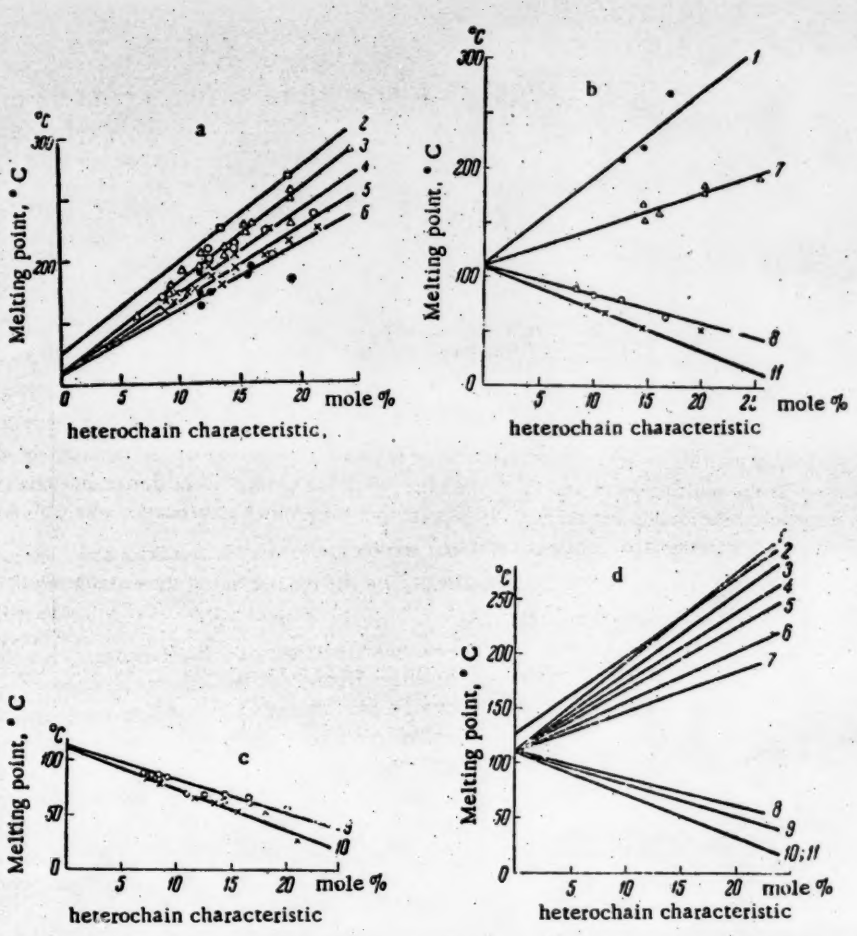


Fig. 1. Change in melting point in the series: 1) polyureas, 2) polyamides with an even number of CH_2 groups in the diamine and acid, 3) the same based on more precise data, 4) polyamides from diamines with an even and acids with an odd number of CH_2 groups, 5) polyamides from diamines with an odd and acids with an even number of CH_2 groups, 6) polyamides from diamines and acids with odd numbers of CH_2 groups, 7) polyurethans, 8) polyanhydrides with an even number of CH_2 groups per unit, 9) polyesters from glycols and acids with even numbers of CH_2 groups, 10) the same with an odd number of CH_2 groups in the acid, 11) polyanhydrides with an odd number of CH_2 groups per unit.

In the case of the polyesters, just as in the case of the polyanhydrides, the melting point decreases with an increase in the heterochain characteristic; this is in contrast to the polyamides, polyurethans, and polyureas where the reverse relationship holds. Apparently, this difference between the polyesters and polyanhydrides, on the one hand, and all polymers containing nitrogen in the chain, on the other hand, is determined by the circumstance that the amide groups, owing to a tendency toward the formation of hydrogen bonds, increase, as they accumulate in the molecule, the strength of the bonds between the individual chains, and this is expressed in an increase in melting point. On the contrary, polyesters and polyanhydrides, which have ester oxygen bonds, decrease

in melting point with an increase in heterochain characteristic, i.e., with an accumulation of ether bonds in the chain. The ether bond is a factor which "softens" the structure of the chain, and an accumulation of ether bonds leads to a decrease in melting point in the polyester and polyanhydride series.

We have set up equations for each of the groups of compounds under consideration, these equations being presented in Table 1. These equations were derived from the usual two-point form for the equation of a straight line. As is well known, in this equation the coefficient of x represents the tangent of the angle made by the line with the abscissa axis, and the constant represents the point of intersection of the line with the ordinate axis. As is seen from Fig. 1, a - c, the experimental points lie rather well on the respective straight lines constructed from the equations presented in Table 1.

TABLE 1

Equations for Various Polymers

Polymer No.	Polymer groups	Equation
1	Polyamides with an even number of methylene groups per unit	$y = 7x + 110$
2	Same	$y = 7x + 125$*
3	Polyamides from dicarboxylic acids with an odd and diamines with an even number of methylene groups	$y = 6.2x + 110$
4	Polyamides from dicarboxylic acids with an even and diamines with an odd number of methylene groups	$y = 5.6x + 110$
5	Polyamides from dicarboxylic acids and diamines with an odd number of methylene groups	$y = 4.5x + 110$
6	Polyamides with sulfide sulfur in the chain	$y = 3x + 110$
7	Polyamides with ether oxygen in the chain	$y = 1.9x + 110$
8	Polyureas with an even number of methylene groups per unit	$y = 8.4x + 110$
9	Polyurethans with an even number of methylene groups per unit	$y = 3.5x + 110$
10	Polyanhydrides with an even number of methylene groups per unit	$y = -2.5x + 110$
11	Polyanhydrides with an odd number of methylene groups per unit	$y = -3.6x + 110$
12	Polyesters with an even number of methylene groups per unit	$y = -3.0x + 110$
13	Polyesters with an odd number of methylene groups per unit	$y = -3.6x + 110$

* For the case where the melting point is determined dilatometrically.

The slope of the line varies depending on the nature of the heterobond. The line for the polyureas has the greatest slope. Next come the polyamides, first those with an even number of methylene groups and then those with the different combinations of odd units. After this come the polyurethans and then the polyamides containing sulfide sulfur and ether bonds in the chains of macromolecules.

The second group of compounds, for which the slope has a negative value, includes successively the polyanhydrides with an odd number of methylene groups, the polyesters with an even number of methylene groups per unit, and the polyesters and polyanhydrides with an odd number of methylene groups per unit.

It is interesting to note that the lines for the latter two compounds fuse into one, and the points corresponding to these compounds are well expressed by a single line. It should be pointed out that we selected those compounds

for which the heterochain characteristics had average values (especially in the polyester and polyanhydride series), since such a melting point regularity is absent in polyester series with high values of the heterochain characteristic; this is apparently caused by polar effects which are caused, in turn, by the large number of carbonyl groups in the molecules of these polyesters.

As seen from the graph presented in Fig. 1, d, all of the lines expressing the dependence of melting point on heterochain characteristic intersect the ordinate axis at a single point, at 100°, i.e., in a region corresponding to the melting point of polyethylene.

It should be noted that the size of the segment cut on the ordinate axis depends greatly on the method of determining the melting point. Thus, curve 2, which shows the melting point dependence in the series of even polyamides, was constructed on the basis of melting points determined by a dilatometric method. In this case, the melting points lie above the usual values by approximately 15°; the intersection of this curve with the ordinate axis occurs not at 110°, but at 125°.

That the point of intersection of the curve with the ordinate axis does not quite correspond to the usual melting point of polyethylene is readily understood if it is considered that polyethylenes generally do not have a precise melting point. According to various data, it varies within a rather wide interval. Both the breadth of this interval and its position depend on the method of determining the melting point and on the nature of the polyethylene sample investigated, the molecular weight and other characteristics. High-pressure polyethylene has a melting point, which, according to the data of different authors, lies between 104 and 111° [6, 7]; low-pressure polyethylene has a melting point between 124 and 133° [6, 7], while polymethylene prepared by the decomposition of diazomethane melts at 128° [8].

Considering these circumstances, it must be admitted that there is rather good correspondence between the conclusions formed from the above equations and the experimental data.

The existence of a linear relationship between the melting points of the groups of polymers which we are considering and their heterochain characteristics shows that there is a direct relationship between the physical properties and the structure of these polymers.

LITERATURE CITED/

[1] V. V. Korshak and T. M. Frunze, Proc. Acad. Sci. USSR 97, 261 (1954).

[2] G. Champetier and R. Aelion, Bull. Soc. Chim. (France) 15, 683 (1948).

[3] R. Hill and E. E. Walker, J. Polymer Sci. 3, 609 (1948).

[4] V. V. Korshak and T. M. Frunze, Bull. Acad. Sci. USSR, Div. Chem. Sci. 756, 762 (1955).•

[5] V. V. Korshak, The Chemistry of High-Molecular Compounds •• (Izd. AN SSSR, 1950), p. 341.

[6] E. Grams and E. Gaube, Angew. Chem. 67, 541 (1955).

[7] S. L. Aggarwal and O. J. Sweeting, Chem. Rev. 57, 723 (1957).

[8] V. V. Korshak and V. A. Sergeev, Proc. Acad. Sci. USSR 115, 308 (1957).•

Institute of Heteroorganic Compounds
Academy of Sciences, USSR

Received April 14, 1958

• Original Russian pagination. See C. B. Translation.

•• In Russian.

ON SUBSTITUTION REACTIONS IN THE METHYLENE UNIT OF β-KETOACETALS

N. K. Kochetkov and E. E. Nifant'ev

(Presented by Academician A. N. Nesmeianov, March 10, 1958)

In recent times, β-ketoacetals have found widespread application in organic synthesis. The high availability of these compounds is due to well-developed methods for their synthesis from β-chlorovinyl ketones [1, 2] and hydroxymethyleneketones [3]. The β-ketoacetals, recently prepared in our laboratory [4], are especially convenient in view of their high stability.

Up to the present, for synthesis purposes use has been made only of condensations at the keto group of acetals [2, 4-6] or of conversions of the type undergone by β-dicarbonyl compounds, chiefly for the synthesis of heterocyclic compounds (see, for example, [1, 7]). Substitution in the methylene group of β-ketoacetals is an especially interesting reaction permitting the use of these acetals in a completely new direction and thereby broadening to a still greater degree the use of β-chlorovinylketones [8], of which β-ketoacetals are analogs and derivatives.

In the present article, we report some preliminary data on reactions of this type. First of all, we studied the bromination of β-ketoacetals under various conditions. In aqueous medium and in the presence of barium carbonate, the bromination of the methylene group of β-ketoacetals proceeds readily; however, the reaction is complicated by cleavage of the acetal group, which results in the formation of meso-substituted β-ketoaldehydes; in individual cases, the latter have also been obtained by bromination of hydroxymethyleneketones [9]:

$$CH_3COCH_2CH(OCH_3)_2 \xrightarrow[H_2O]{Br_2} CH_3COCHBrC\begin{matrix}O\\ \diagdown\\ \diagup\\ H\end{matrix}$$

A more interesting result was obtained by bromination of cyclic acetals in ether in the presence of barium carbonate; in this case also, bromination proceeded in the methylene group, but the acetal group was retained:

$$RCO-CH_2CH\begin{matrix}O-CH_2\\ \diagdown\\ \diagup\\ O-CH_2\end{matrix} \xrightarrow{Br_2} R-CO-CHBr-CH\begin{matrix}O-CH_2\\ \diagdown\\ \diagup\\ O-CH_2\end{matrix} \qquad R = CH_3-;\ C_6H_5-$$

The resulting bromoacetals may be used in various directions; however, one of the most interesting possibilities is dehydrobromination by the action of potassium hydroxide in benzene, a reaction which we carried out:

$$C_6H_5CO-CHBr-CH\begin{matrix}O-CH_2\\ \diagdown\\ \diagup\\ O-CH_2\end{matrix} \xrightarrow{KOH} C_6H_5CO-CH=C\begin{matrix}O-CH_2\\ \diagdown\\ \diagup\\ O-CH_2\end{matrix}$$

It may be hoped that this reaction will open up possibilities for the preparation of the most varied acetals of β-acylketones, compounds for which there is at present no satisfactory general method of synthesis. The action of an excess of alcoholic alkali on meso-bromoketoacetals results in the formation of esters of β-keto acids, which are formed as a result of the further conversion of the acetal of β-acetalketene:

$$CH_3COCHBr-CH(OCH_3)_2 \xrightarrow[CH_3OH]{KOH} CH_3COCH_2-COOCH_3.$$

Another reaction of β-ketoaldehydes, the study of which was recently undertaken by us, is oxidation with lead tetraacetate. When the dimethyl acetal of acetoacetaldehyde is heated with this reagent in benzene or acetic acid solution, oxidation of the acetal occurs at the methylene group, but the reaction is complicated by replacement of one of the alkoxyl radicals by an acetoxy group:

$$CH_3COCH_2-CH(OCH_3)_2 \xrightarrow[CH_3COOH]{Pb(OCOCH_3)_4} CH_3-CO-\underset{OCOCH_3}{\overset{OCOCH_3}{CH}}-\underset{OCH_3}{CH}$$

The replacement of alkoxyl radicals in acetals by an acyloxy group under analogous conditions is well known [10]. During the time this work was being carried out, a brief note by Plieninger and Müller appeared in which results similar to ours were reported without any indication of the experimental details or constants of the compounds prepared.

Besides the reactions described above, we also studied the condensation of the cyclic acetal of benzoylacetaldehyde with benzaldehyde. The interaction of these two reagents in methanol in the presence of gaseous hydrogen chloride gave β-chloro-β-phenylpropiophenone, the structure of which was shown by conversion to 3,5-diphenylisoxazoline. Thus, the condensation of an acetal through the methylene group with benzaldehyde was complicated by decomposition of the acetal in the manner of β-dicarbonyl compounds, since the reaction was carried out under rather severe conditions:

$$C_6H_5COCH_2-\underset{O-CH_2}{\overset{O-CH_2}{CH}} \xrightarrow[HCl]{C_6H_5C\overset{O}{\underset{H}{<}}} \left[C_6H_5-CO-\underset{\underset{C_6H_5}{|}}{\overset{\overset{O-CH_2}{|}}{CH}}-\underset{O-CH_2}{\overset{O-CH_2}{CH}}\right] \longrightarrow$$

$$\longrightarrow C_6H_5COCH_2-\underset{C_6H_5}{\overset{Cl}{CH}}$$

In attempts to carry out nitrosation and sulfonation of β-ketoacetals, we were unable to obtain the desired results.

The preliminary data reported in this article show that the activity of the methylene group in β-ketoacetals can hardly compare with the activity of the methylene group of other β-dicarbonyl compounds; it is more reminiscent of the activity of the α-carbon group in ordinary ketones.

EXPERIMENTAL*

Bromination of the dimethyl acetal of acetylacetaldehyde in water. To a mixture of 7 g of the acetal, 5.2 g of barium carbonate, and 15 ml of water was added dropwise 2.9 ml of bromine while stirring and illuminating with a lamp; the reaction mixture was gradually heated on a water bath to initiation of the reaction.

* With the assistance of N. V. Molodtsov and V. N. Kulakov.

After the addition of half of the total amount of bromine, the temperature of the reaction mixture had risen to 55-60°; hence, heating was discontinued. After complete decolorization of the reaction mixture, the lower layer was separated. The aqueous layer was extracted three times with ether. The ether extracts were combined with the separated oil and dried over sodium sulfate. After careful distillation of the ether under vacuum, the crystalline material remaining in the flask was pressed on a porous filter, washed once with 1-2 ml of chloroform and with petroleum ether (3 times with 4 ml). The material was dried in a vacuum desiccator. The yield was 4.4 g (51 %).

The α-bromo-β-ketobutyraldehyde crystallized in light rose plates with a m. p. of 109-110°. It darkened on standing.

Found %: C 28.61, 28.66; H 3.17, 3.14. $C_4H_5O_2Br$. Calculated %: C 29.05; H 3.15.

Bromination of the ethylene glycol acetal of acetylacetaldehyde in ether. To a mixture of 26.2 g of the acetal, 40 g of barium carbonate, and 70 ml of ether was added dropwise 10.5 ml of bromine while stirring and under illumination from a lamp. The reaction was very slow for the first 5-7 minutes, but then proceeded vigorously. When the bromine had been completely added, the reaction mixture was stirred for an additional 1-2 minutes. The suspended mineral matter was filtered and carefully washed with ether. The ether filtrate was carefully dried over sodium sulfate. After distillation of the ether, the residue was distilled under vacuum, and the fraction boiling at 104-107°/6 mm was collected. The yield was 17 g (41 %). After a second distillation, the material had the following constants: b. p. 104-104.5°/6 mm, $n^{20}D$ 1.4938, d^{20}_4 1.5840, $MR_{D\,found}$ 38.50, MR_{calc} 38.77.

Found %: C 34.19, 34.14; H 4.29, 4.31. $C_6H_9O_3Br$. Calculated %: C 34.41; H 4.30.

Colorless oil with sharp odor. Unstable on standing.

The interaction of the ethylene glycol acetal of meso-bromoacetylacetaldehyde with alcoholic alkali. 4 g of the bromoacetal, 1.1 g of potassium hydroxide, and 13 ml of methanol were mixed in the cold and then heated on a water bath for 2 hours. The mineral material was suction filtered, and the resulting oil was distilled under vacuum. The fraction boiling at 65-73°/10 mm (1.8 g) was distilled a second time, and the methyl ester of acetoacetic acid was collected at 69-70.5°/10 mm. The material had $n^{20}D$ 1.4183, d^{20}_4 1.0769. Literature values [12]: b. p. 73-74°/12 mm, $n^{20}D$ 1.4186, d^{20}_4 1.0769.

Found %: C 51.74, 51.60; H 6.98, 7.04. $C_5H_8O_3$. Calculated %: C 51.81; H 6.92.

Ethylene glycol acetal of β-benzoylketene. 4 g of the acetal of meso-bromobenzoylacetaldehyde, 20 ml of absolute benzene, and 1.3 g of powdered potassium hydroxide were stirred first without heating and then at 70-80° for 4 hours; the organic layer was decanted, and the benzene was distilled from it under vacuum. The remaining oil was diluted with half its volume of ether, and the mixture was cooled to 70°. The precipitated crystals were quickly filtered by suction and washed with cold ether. The yield of ethylene glycol acetal of benzoylacetaldehyde was 0.75 g (27%). After recrystallization from chloroform, the colorless needles melted at 61-61.5°.

Found %: C 69.21, 69.08; H 5.80, 5.87. $C_{11}H_{10}O_3$. Calculated %: C 69.42; H 5.41.

Bromination of the ethylene glycol acetal of benzoylacetaldehyde. 5 ml of bromine was added dropwise, with stirring and illumination from a lamp, to a solution of 15 g of the acetal in 250 ml of absolute ether. On completion of the addition of the bromine, the reaction mixture was stirred for another 15 minutes; the ether was then distilled, and, on some days, the residue remained in the condenser where it crystallized. The crystals were pressed on a porous plate and recrystallized from methanol. The yield was 8.4 g (50 %), m. p. 66-67°.

Found %: C 48.77, 48.77; H 4.20, 4.22. $C_{11}H_{11}O_3Br$. Calculated %: C 48.71; H 4.06.

Oxidation of the dimethyl acetal of acetylacetaldehyde with lead tetraacetate. 12 g of the acetal was added dropwise to a suspension of 41 g of lead tetraacetate in 30 ml acetic acid while stirring and heating to 60°. The addition of the acetal was completed in 20 minutes, and the temperature of the reaction mixture was raised to 70-80°. After 1.5 hours, the temperature was decreased to 65°, and the reaction mixture was stirred for another 5 hours, after which it was cooled. The mineral material was filtered and washed with ether, the combined organic filtrates were treated with water, and the aqueous layer was extracted with ether. The ether extract was dried with sodium sulfate, the ether was distilled, and the residue was distilled under vacuum; the

fraction boiling at 67-69°/15 mm (3 g), the original acetal, and the fraction boiling at 142-145°/15 mm, α-, β-acetoxy-β-methoxy methyl ethyl ketone [3,4-diacetoxy-4-methoxy-2-butanone], were collected. The yield was 5.2 g (35% calculated on the reacted acetal). After a second distillation, the material had the following constants: b. p. 144-145°/15 mm, n^{20}_D 1.4334, d^{20}_4 1.1460.

Found %: C 49.71, 49.54; H 7.03, 6.94. $C_9H_{14}O_6$. Calculated %: C 49.52; H 6.47.

Interaction of the ethylene glycol acetal of benzoylacetaldehyde with benzaldehyde. Dry hydrogen chloride was passed for 2-3 minutes into a mixture of 3 g of the acetal, 5 g of benzaldehyde, and 5 ml of methanol. The reaction was very exothermic. After the contents of the flask had been cooled, a voluminous white precipitate formed; this was suction filtered and washed with a small amount of methanol. The yield of β-chloro-β-phenylpropiophenone was almost quantitative; m. p. 114.5-115.5°.

Found %: C 73.72, 73.77; H 5.42, 5.49. $C_{15}H_{13}OCl$. Calculated %: C 73.45; H 5.30.

With hydroxylamine, this substance formed 3,5-diphenyloxazoline with a m. p. of 74-74.5°.

The literature value for 3,5-diphenyloxazoline [12]: m. p. 73°.

LITERATURE CITED

[1] A. N. Nesmeianov, N. K. Kochetkov, and M. I. Rybinskaia, Bull. Acad. Sci. USSR, Div. Chem. Sci. 395 (1951).

[2] C. Price and L. Pappallardo, J. Am. Chem. Soc. 72, 2613 (1950).

[3] R. Royals and B. Branock, J. Am. Chem. Soc. 75, 2050 (1953).

[4] N. K. Kochetkov, E. E. Nifant'ev, and A. N. Nesmeianov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 949 (1957).*

[5] N. K. Kochetkov, E. E. Nifant'ev, and A. N. Nesmeianov, Proc. Acad. Sci. USSR 104, 422 (1956).*

[6] C. H. Shank, K. F. Folkers, et al., J. Am. Chem. Soc. 79, 3294 (1957).

[7] N. K. Kochetkov, Proc. Acad. Sci. USSR 84, 289 (1952).

[8] N. K. Kochetkov, Prog. Chem. 24, 32 (1955).

[9] M. S. Matta, K. Kaushal, and S. S. Deshapande, J. Ind. Chem. Soc. 23, 454 (1946).

[10] W. Bruchel and C. Bancroff, Am. J. Sci. (4), 44, 371 (1917).

[11] H. Plieninger and F. Müller, Angew. Chem. 68, 618 (1956).

[12] H. Rupe and F. Schneider, Ber. 28, 957 (1895).

M. V. Lomonosov Moscow State University

Received March 8, 1958

* Original Russian pagination. See C. B. Translation.

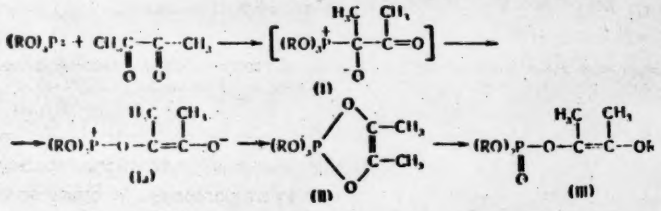
ON SOME NEW TYPES OF THE ARBUZOV REARRANGEMENT

V. A. Kykhtin

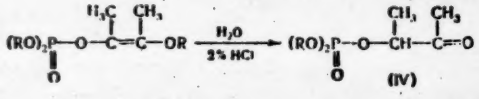
(Presented by Academician B. A. Arbuzov, March 14, 1958)

In recently published papers by G. Kamai and V. A. Kukhtin there are described some new instances of the Arbuzov rearrangement which take place during the action of various electrophilic reagents on trialkyl phosphites [1-8]. The majority of these papers were devoted to the study of the interaction of esters of phosphorous and phosphonous acids with C=C−C=O-conjugated systems [3-8].

Continuing the study of reactions of π,π-conjugated systems with trialkyl phosphites, we found that the latter readily enter into reaction with diacetyl, the final product of this reaction being a dialkoxy (dimethylalkoxyvinyl) phosphate (III). By analogy with previously studied reactions [3, 4], its formation evidently proceeds according to the following scheme:

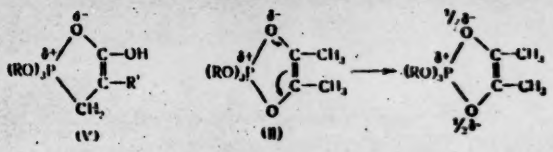


The product (I), formed by the nucleophilic attack by the phosphorus on the carbon atom, readily rearranges to product (Ia) with the formation of the more stable P−O bond. Bengelsdorf [9] was led to such a scheme for the case of the interaction of phosphites with α-halocarbonyl compounds. The constants of the alkoxyvinyl phosphates obtained are presented in Table 1. On complete saponification, these substances yield phosphoric acid, but on careful saponification with a 2% solution of hydrochloric acid, the corresponding keto phosphates are formed (Table 1).



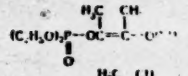
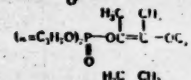
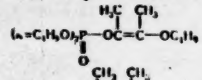
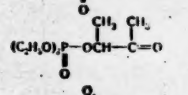
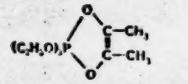
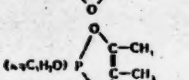
By carrying out the addition of trialkyl phosphites to diacetyl under mild conditions (20-30°, in ether solution), we were able to separate in the pure form, by distillation, the intermediate reaction product (II). In its properties, it was analogous in many respects to the impure form of the intermediate product of the addition of trialkyl phosphites to α, β-unsaturated acids, previously studied by us [3-8]. It reacted with water with considerable evolution of heat (to 50-70°), forming the keto phosphate (IV). It converted to the final alkoxyvinyl phosphate (III) on heating or spontaneously on standing. Telomerization proceeded vigorously when several drops of product (II) were added to acrylic acid [8].

The reason for the high stability of our trialkoxyphospho (dimethylethylene) dioxides (II) in comparison with the intermediate products of the addition of phosphites to acids becomes clear when their formulas are compared:



As shown in our papers [7, 8], the P—O bond in the cyclic product (V) has an ionic character, and if it is not completely ionic, it is, in any case, strongly polarized and unstable. The molecule of product (II) is symmetrical; the two P—O bonds are equivalent, and the polarization is obviously equally distributed between the two bonds thereby providing for stability of the molecule. However, at the instant of reaction, polarization is probably concentrated at the bond being attacked, and, therefore, product (II) is not inferior to product (V) in chemical activity.

TABLE 1

Formula	B. p., °C/mm Hg	n_D^{20}	d_4^{20}	P, % found	P, % calc.	Yield, %
	127—130/10	1,4250	1,1061	12,32	12,30	23,3
	140—142/10	1,4230	1,0752	11,17	10,51	46,7
	148—150/10	1,4240	1,0192	9,83	9,63	42,6
	132—134/12	1,4230	1,1122	13,78	13,84	30,7
	104—105/10	1,4290	1,0825	12,42	12,30	47,2
	127—130/10	1,4305	1,0256	10,92	10,51	37,1

The isolation in the chemically pure form of the intermediate product of the addition of trialkyl phosphites to diacetyl is again confirmation that the interaction of π,π-conjugated systems with esters of trivalent phosphorus acids is a new type of the Arbuzov rearrangement. It is true that a phosphate, and not an alkylphosphonic acid, is formed as the result of the addition to diacetyl. However, the almost complete analogy of the course of this reaction to the action of C=C—C=O-conjugated systems compels us to consider it as one of the types of the Arbuzov rearrangement.

In recent years, many authors have studied the reaction of α-halocarbonyl compounds with phosphites [9-14]. In our own papers, we have already expressed the thought that the reaction of σ,π-conjugated systems with phosphites, as well as reactions of π,π-conjugated systems, can be considered to be a particular case of the Arbuzov rearrangement [3, 4]. The conjugated system in halocarbonyl compounds is analogous in nature to the conjugated system of α-diketones.

Therefore, the obtaining of the intermediate product of the Arbuzov rearrangement occurring during the action of diacetyl on trialkylphosphites is, in our opinion, indirect confirmation of our proposal that the reaction

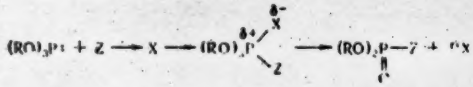
π,π-conjugation σ,π-conjugation

of halocarbonyl compounds with phosphites proceeds according to the scheme of the Arbuzov rearrangement. It must also be noted that, independently of us, A. I. Razumov was led to the conclusion that extension of the concept of the Arbuzov rearrangement is necessary [15]. In connection with the above, we consider it necessary and timely to propose a new, broader definition of the Arbuzov rearrangement. It seems to us that, on the basis of our experimental data, on the basis of the work on α-halocarbonyl compounds [9-14], and on the basis of certain other work [16-19], it is possible to formulate a definition of the Arbuzov rearrangement along the following lines.

By the Arbuzov rearrangement is meant the transformation of esters of trivalent phosphorus acids into derivatives of pentavalent phosphorus, the reaction proceeding by the action of electrophilic reagents and being accompanied by the formation of a new bond P—Z (Z = C, O, N, and others). It proceeds by means of an initial attack by the nucleophilic trivalent phosphorus atom on the most electrophilic part of the molecule; subsequently an intermediate addition product is formed, which is converted into the final product by the splitting off of an ester radical from the nucleophilic part of the addition product.

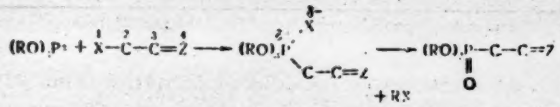
Presently known cases of the Arbuzov rearrangement can be divided into three types:

1. Rearrangement under the action of nonconjugated (or σ,σ-conjugated) electrophilic systems:

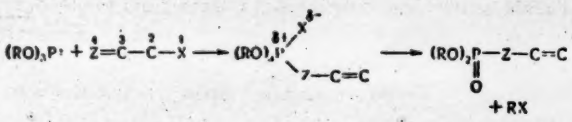


2. Rearrangement under the action of σ,π-conjugated systems. This can proceed in two directions:

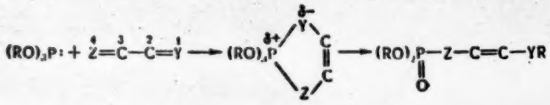
a) according to a 2-1 scheme (without transfer of the reaction center):



b) according to a 4-1 scheme [or (3)-4-1, if the initial attack is considered to be at C_3 with subsequent formation of the P—Z bond], i.e., with transfer of the reaction center:



3. Rearrangement under the action of π,π-conjugated systems. It always proceeds with transfer of the reaction center according to a 4-1 or (3)-4-1 scheme.



Further study and consideration of these interesting reactions will undoubtedly permit additions to and an increase in the accuracy of our definition.

K. M. Orekhov participated in the experimental part of this work, and the author considers it his privilege to express his appreciation for this assistance.

LITERATURE CITED

[1] Gil'm Kamai and V. A. Kukhtin, Proc. Acad. Sci. USSR 102, 283 (1953); J. Gen. Chem. 27, 949 (1957).*

* Original Russian pagination. See C. B. Translation.

[2] Gil'm Kamai, V. A. Kukhtin, and O. A. Strogova, Trans. Kazan Chem. Technology Inst. 21, 155 (1956).

[3] Gil'm Kamai and V. A. Kukhtin, Proc. Acad. Sci. USSR 109, 91 (1956);* Proc. Acad. Sci. USSR, Chem. Div. 112, 867 (1957).*

[4] Gil'm Kamai and V. A. Kukhtin, J. Gen. Chem. 27, 2372, 2376 (1957).*

[5] Gil'm Kamai and V. A. Kukhtin, Trans. Chem. Technology Inst. 23, 133 (1957).

[6] Gil'm Kamai and V. A. Kukhtin, J. Gen. Chem. 28, 941 (1958).*

[7] V. A. Kukhtin and Gil'm Kamai, J. Gen. Chem. 28, 1216 (1958).*

[8] V. A. Kukhtin, Gil'm Kamai, and L. A. Sinchenko, Proc. Acad. Sci. USSR, Chem. Div. 118, 3 (1958).*

[9] L. Bengelsdorf, J. Org. Chem. 21, 475 (1956).

[10] A. N. Pudovik and N. M. Lebedeva, Proc. Acad. Sci. USSR 101, 689 (1956).*

[11] W. Perkow, E. Krockow, and K. Knoevenagel, Ber. 88, 662 (1955).

[12] W. Perkow, Ber. 87, 755 (1954).

[13] F. Allen and O. Jonson, J. Am. Chem. Soc. 77, 1871 (1955).

[14] A. N. Pudovik and L. G. Biktemirova, J. Gen. Chem. 27, 1708 (1957).*

[15] A. I. Razumov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 122 (1958).*

[16] N. Kreutzkampf, Naturwiss. 43, 81 (1956).

[17] R. Connel and H. W. Coower, J. Am. Chem. Soc. 78, 4453 (1956).

[18] H. W. Coower, M. McColl, and J. Dicey, J. Am. Chem. Soc. 79, 1963 (1957).

[19] I. Allen, J. Am. Chem. Soc. 79, 3071 (1957).

Kazan Affiliate
All-Union Cinema and Photographic
Scientific Research Institute

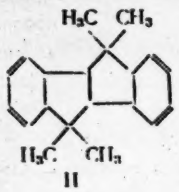
Received March 11, 1958

* Original Russian pagination. See C. B. Translation.

ON THE ALKYLATION OF BENZENE AND ITS HOMOLOGS WITH ACETIC ACID ESTERS OF γ-ACETYLENIC GLYCOLS

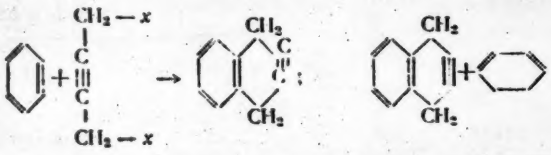
R. M. Lagidze, N. K. Iremadze, Sh. D. Kuprava, and
Corresponding Member AN SSSR A. D. Petrov

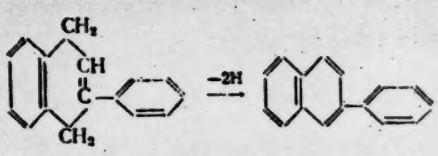
Over the course of the past few years, we have studied the alkylation of benzene with butynediol and with various of its homologs [1-6]. A series of polycyclic aromatic hydrocarbons were synthesized by this method; however, owing to inaccuracies in the determinations of the molecular weights (determined cryoscopically in benzene) and for other reasons, we ascribed incorrect structures to these compounds. In [7], we corrected the admitted inaccuracy, and acknowledged the first of these hydrocarbons synthesized by us to be 2-phenylnaphthalene (I). At the same time, we presented an hypothetical scheme for the formation of 2-phenylnaphthalene. We sent a copy of our article to Prof. Hancock (Reed College, Portland, Oregon, U.S.A.), who is also studying the alkylation of aromatic hydrocarbons with butynediols and with whom we carry on a correspondence. In his answering letter, sent to us in July, 1957, Prof. Hancock acknowledged our new idea on the structure of this hydrocarbon to be correct. He merely proposed another scheme for its formation, according to which, 2,3-diphenyl-1,3-butadiene is first formed, and this, under the influence of HCl, isomerizes to 3-methyl-3-phenylhydrindene which is converted by dehydrogenation and ring expansion under the influence of the Lewis acid into 2-phenylnaphthalene. He also directed our attention to the fact that the second of the hydrocarbons synthesized by us – the product of the alkylation of benzene with tetramethylbutynediol diacetate with a m. p. of 83-84°, which was first obtained by one of us in 1952 [8, 3, 9] – is 5,5,10,10-tetramethyl-4b,5,9b,10-tetrahydroindeno(2,1a)indene, II [10].



II

The formation of 2-phenylnaphthalene, along with acetyltetralin, by the alkylation of benzene with 2-butyne-1,4-diol has also been recently confirmed by Maier [11]. At the present time, the accuracy of our scheme for the formation of hydrocarbon (I) is problematical, just as is that of Hancock's scheme. It seems to us that it is more probable that the formation of this hydrocarbon proceeds according to the scheme:





As regards the structure of the above-indicated hydrocarbon with a m. p. of 83-84°, on the basis of molecular weight determinations (Rast method), a comparison of the appropriate properties, the preparation of the dibromide with a m. p. of 312-313°, and an investigation of its spectrum, we have come to the conclusion that, as proposed by Hancock, structure (II) must be assigned to it, and that its homologs must have structures analogous to the structures of homologs of hydrocarbon (II) [9].

In the present work, we studied the anhydrous $AlCl_3$-catalyzed condensation of: 1) 2,5-dimethyl-3-heptyne-2,5-diol diacetate with toluene, 2) the monoacetate of di(1-hydroxycyclohexyl) acetylene with toluene, and 3) tetramethylbutynediol diacetate with toluene and p-xylene.

I. In agreement with the literature data [12], the 2,5-dimethyl-3-heptyne-2,5-diol synthesized by us had a m. p. of 43-45°. Acetylation of this diol with acetic anhydride under previously described conditions gave the diacetate with a b. p. of 97-100°/ 2-3 mm; d^{20}_4 0.9065; n^{20}_D 1.4531 (yield, 60% of theoretical). It saponified with 2.22 ml of 0.5 N alcoholic KOH; $C_{13}H_{20}O_4$. The calculated value is 2.26 ml. A qualitative test for the acetylenic triple bond gave a positive reaction.

To a mixture of 60 g of benzene (0.769 mole) and 12.4 g of anhydrous $AlCl_3$ (0.094 mole), which was cooled with ice water, 10 g of the diacetate was added dropwise over a period of 40 minutes. The temperature was held in the range 5-10°. The flask was then gradually heated on a water bath. Appreciable liberation of HCl began at about 40-45°; this continued for a brief time, and began again with an increase in the temperature. After this, the reaction was carried out at 70-80° for approximately 2 hours. Treatment of the complex by the usual method gave 11.57 g of condensation product; multistage fractionation gave 3.58 g of a fraction with a b. p. of 80-85°/ 1-2 mm, d^{20}_4 0.9964, n^{20}_D 1.4775. An identical product was obtained by the interaction of free $AlCl_3$ directly with the diacetate in dearomatized ligroin when the reacting substances were taken in equimolar amounts, and the reaction was carried out by heating the mixture at 75-80° for about 2 hours. The fraction boiling at 80-85°/ 1-2 mm corresponded to 3-chloro-4-acetoxy-2,5-dimethyl-2,4-heptadiene.

Found %: Cl 16.28, 16.61; M 212.06, 217.65. $C_{11}H_{17}O_2Cl$. Calculated %: Cl 16.4; M 216.5.

0.7 g of the substance was dissolved in 60 ml of glacial acetic acid and oxidized with 3.5 g of CrO_3 over a 4-hour period. The reaction mixture was diluted with water, and part of the liquid was distilled. The first portions of the distillate were treated with 2,4-dinitrophenylhydrazine. Fractional precipitation of the precipitate gave a product which had a m. p. of 125-127° and which caused no m. p. depression when mixed with the 2,4-dinitrophenylhydrazone of acetone, which has a m. p. of 125-126° [13]; a substance with an m. p. of 115-116° was also obtained, and this caused no m. p. depression when mixed with the 2,4-dinitrophenylhydrazone of methyl ethyl ketone [13]. The major part of the solution was extracted with ether (5 times with 30 cc), the solvent was distilled, and the residue was sublimed at 130-140° over a period of 3 hours. The resulting sublimate had a m. p. of 99-101° after recrystallization from ethyl alcohol, and a mixture with pure oxalic acid showed no depression of the melting point.

The fraction (2.76 g) with a b. p. of 170-172°/1-2 mm, d^{20}_4 1.0440; n^{20}_D 1.5825, corresponded to the hydrocarbon $C_{21}H_{24}$ (III) (yield, 24% of theoretical). From the products of its oxidation with CrO_3 in glacial acetic acid under the conditions described above, methyl ethyl ketone and benzoic acid were isolated and identified. It displayed properties similar to those of the other hydrocarbons prepared by this route. Brief oxidation of (III) (see Table 1) with CrO_3 in glacial acetic acid over a period of 30-40 minutes gave a neutral, crystalline material with a m. p. of 144-145°.

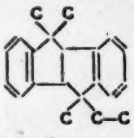
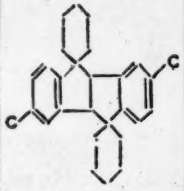
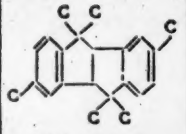
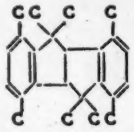
Found %: C 81.55, 81.50; H 7.18, 7.27; M 318.4, 324.3. $C_{21}H_{22}O_2$. Calculated %: C 82.35; H 7.18.

Bromination in cold CCl_4 of the fraction boiling at 170-172°/1-2 mm gave a dibromide with a m. p. of 248-249°.

Found %: Br 37.17. $C_{21}H_{22}Br_2$. Calculated %: Br 36.86.

II. Condensation of the monoacetate of di(1-hydroxycyclohexyl)-acetylene with toluene under analogous conditions gave a hydrocarbon of the composition $C_{28}H_{34}$ (IV) (Table 1). It crystallized immediately after removal of the solvent from the condensation product. After two-fold recrystallization (from a 2:1 mixture of alcohol and benzene), the product had an m. p. of 250-251° and was characterized by properties similar to those of the previously described hydrocarbons (yield, 10-12% of theoretical).

TABLE 1

Hydrocarbon	Formula	Analysis	found %	calc. %	In n-heptane λ_{max} mμ	log ϵ_{max}
Hydrocarbon (III) $C_{21}H_{24}$, b. p. 170—172°/1—2 мм		C	91,2; 91,03	91,30	260	3,49
		H	8,60; 8,65	8,69	266	3,52
		M	273; 276	276	273	3,51
		MR	—88,29	—87,5		
Hydrocarbon (IV) $C_{28}H_{34}$, b. p. 250—251°		C	90,87; 90,94	90,81	(265)	(3,21)
		H	9,37; 9,38	9,18	271	3,42
		M	373,8; 363,6		278	3,52
Hydrocarbon (V) $C_{22}H_{26}$, b. p. 138—140°/1 мм		C	90,47; 90,61	91,03	258	3,40
		H	9,22; 9,14	8,96	272	3,49
		M	280; 285	290		
		MR	—93,11	—92,19	278	3,51
Hydrocarbon (VI) $C_{24}H_{30}$, b. p. 136—137°		C	90,27; 90,56	90,56		
		H	9,52; 9,68	9,43	267	2,71
		M	316	318		

III. Condensation of tetramethylbutynediol diacetate with toluene. Amounts of the reactants: 30 g (0.131 mole) of the diacetate, 36 g (0.270 mole) of anhydrous $AlCl_3$, 88 g (0.956 mole) of toluene. The condensation time was 8 hours. The maximum temperature at the conclusion of the reaction was 97-100°. Along with other substances which still have not been investigated, multistage fraction of the condensation product gave an incompletely pure product with a b. p. of 138-140° (1 mm), d^{20}_4 1.0099; $n^{20}D$ 1.5670, which had the approximate composition $C_{22}H_{26}$ (V) (yield, 20% of theoretical). In chemical behavior, it was similar to the hydrocarbons mentioned above. On standing, it oxidized appreciably, acquiring a yellow color.

IV. Condensation of tetramethylbutynediol diacetate with p-xylene. The p-xylene used in the reaction was twice distilled over metallic sodium, b. p. 134°/730 mm, $n^{20}D$ 1.4950; freezing point +13° [14]. The reaction was carried out under the conditions described above by gradually heating the flask (after the addition of the diacetate) to 100° over a period of 1 hour. From 20 g of the diacetate was obtained 19.78 g of condensation product, distillation of which gave three broad fractions. The higher-boiling fraction, b. p. 170-190°/2-3 mm, 4.1 g, almost completely crystallized on the addition of a small amount of acetone. Several recrystallizations from ethanol gave a product with a m. p. of 136-137°; it closely corresponded to the hydrocarbon of the composition $C_{24}H_{30}$ (VI). The u.v. spectra and the structures of the hydrocarbons synthesized by us are presented in Table 1.

The spectra of hydrocarbon (VI) had the same character as those of (II), (III), (IV), and (V), but the bands in the 260 mμ region, which are characterized by fine structures, were absent. This apparently means that the intensity of the 260 mμ band of (II) was low. The intensity of the band was low in comparison with the intensities

of the bands of hydrocarbons (III), (IV), and (V). Such a change in the absorption spectra with the introduction of additional methyl groups is, perhaps, connected with deformation of some of the valence angles of the molecule. The presence in the spectra of hydrocarbons (III) and (V) of an absorption band in the 295 mμ region is apparently due to the presence of a very small amount of impurities.

I. r. spectra were obtained for (III) and also for its dehydrogenation product – a hydrocarbon with a m. p. of 216° [6, 9]. (IKS-11 spectrometer with NaCl prism: in CCl_4 and CS_2 solutions). The following bands were observed (in cm^{-1}): (III) – 725 (av), 762 (vs), 790 (w), 809 (av), 820 (w), 867 (av), 895 (av), 916 (w), 942 (s), 977 (w), 1012 (vs), 1026 (s), 1080 (av), 1112 (av), 1132 (w), 1155 (s), 1188 (av), 1228 (s), 1257 (w), 1284 (s), 1321 (av), 1363 (s), 1375 (vs), 1423 (w), 1446 (vs), 1474 (w), 1580 (w). For the hydrocarbon with a m. p. of 216-217°: 710 (av), 753 (vs), 762 (w), 786 (w), 857 (s), 928 (av), 986 (s), 1010 (s), 1072 (s), 1110 (av), 1144 (av), 1168 (w), 1214 (s), 1248 (s), 1298 (av), 1330 (w), 1360 (s), 1368 (s), 1458 (vs), 1605 (s). The general character of the i. r. spectrum of (III) was similar to that of the spectrum previously obtained for (II); in particular, bands in the regions 730-760 cm^{-1}, 950-1050 cm^{-1}, and 1480-1580 cm^{-1} are characteristic. Moreover, two bands were observed at 1363-1375 cm^{-1}, corresponding to gem-substituted CH_3 groups. It is interesting to note that on going to the hydrocarbon with an m. p. of 216-217°, the frequency for the gem-substituted C atom was retained, but new frequencies appeared which are usually assigned to a monosubstituted aromatic ring: 710, 1010, 1072, and 1605 cm^{-1}. Along with these bands, in the spectrum of the hydrocarbon with a m. p. of 216-217° was observed an intensity band at 753 cm^{-1}, which is encountered in the spectrum of (III) and other 1,2-substituted benzenes.

The ultraviolet absorption spectra were taken by T. N. Shkurina, and the infrared by Iu. P. Egorov.

LITERATURE CITED

[1] R. M. Lagidze and A. D. Petrov, Proc. Acad. Sci. USSR 83, 235 (1952).

[2] R. M. Lagidze, Trans. Inst. Chem. Acad. Sci. GeorgSSR 12, 157 (1956).

[3] R. M. Lagidze and N. R. Loladze, Reports of the Acad. Sci. Georg SSR 8, 608 (1955).

[4] R. M. Lagidze and A. I. Dvalishvili, Reports of the Acad. Sci. Georg SSR 3, 205 (1955).

[5] R. M. Lagidze, N. K. Iremadze, and L. P. Chigogidze, J. Gen. Chem. 27, 54 (1956).*

[6] R. M. Lagidze and Sh. D. Kuprava, Proc. Acad. Sci. USSR, Div. Chem. Sci. 110, 795 (1956).*

[7] R. M. Lagidze and A. D. Petrov, Reports of the Acad. Sci. GeorgSSR 3, 279 (1957).

[8] R. M. Lagidze, Doctorate Dissertation, Inst. Gen. Chem. (Moscow, 1952).**

[9] R. M. Lagidze, Material from the Scientific Sessions of the Institutes of Chemistry of the Academy of Sciences of the Transcaucasian Republic [In Russian] (Baku-Erivan, 1956-1957).

[10] S. G. Smith and G. F. Wright, Canad. J. Chem. 32, 729 (1954).

[11] G. Maier, Chem. Ber. 12, 2949 (1957).

[12] A. T. Babaian, Bull. Acad. Sci. ArmSSR 5-6, 10-11, 135 (1941).

[13] R. Shriner and R. Fuson, The Systematic Qualitative Identification of Organic Compounds (The Systematic Identification of Organic Compounds) (Foreign Lit. Press, 1950), p. 259. (Russian Translation).

[14] G. Egloff, Physical Constants of Hydrocarbons 3, p. 75.

N. D. Zelinskii Institute of Organic Chemistry
Academy of Sciences USSR
Institute of Chemistry
Academy of Sciences GeorgSSR

Received April 23, 1958

* Original Russian pagination. See C. B. Translation.
** In Russian.

POLYMERIZATION OF HIGHER DIENIC HYDROCARBONS

I. A. Livshits and L. M. Korobova

(Presented by Academician V. A. Kargin, March 24, 1958)

In recent years, in the Soviet Union and in the U.S.A. isoprene polymers have been synthesized, which, in their combination of properties, approximate natural rubber more than other previously known synthetic rubbers [1-5].

It seemed of interest to determine to what extent high strength in combination with high elasticity, which is characteristic of natural rubber vulcanizates, is also characteristic of polymers of other dienic hydrocarbons. With this aim, polymers of 2-methyl-1,3-pentadiene, 2-ethyl-1,3-butadiene, and 2-isopropyl-1,3-butadiene were synthesized.

2-Methyl-1,3-pentadiene was prepared by catalytic conversion of a mixture of isopropyl alcohol and acetone over an S. V. Lebedev catalyst modified by the method of Iu. A. Gorin and A. A. Vasil'ev [6]. Separation of the diene from its mixture with other hydrocarbons was carried out by rectification in a laboratory column with an efficiency of 100 theoretical plates.

2-Ethyl-1,3-butadiene was prepared by the method by which Marvel and co-workers originally attempted to prepare this hydrocarbon [7] with the exception that the catalyst used for the dehydration of 2-ethyl-2-hydroxy-1-butene was not potassium acid sulfate, but instead was prepared by impregnation of pieces of coke with a solution of sodium phosphate, phosphoric acid, and butylamine phosphate [8].

The yield of 2-ethyl-1,3-butadiene was 32.4% of theoretical. The 2-isopropyl-1,3-butadiene was prepared by the method of Marvel [7, 9].

TABLE 1

Polymerization of Alkylbutadienes

Monomer	Polymerization temp., °C	Polymerization	Polymerization time, hours	Polymer plasticity
2-Ethyl-1,3-butadiene	50	Lithium	5	0.38
	50	"	0.5	0.59
	70	Butyllithium	0.08*	not determined
2-Isopropyl-1,3-butadiene	50	Lithium	4.5	0.37
	70	"	7	0.39
2-Methyl-1,3-pentadiene	50	"	16	0.66
	70	Butyllithium	7	0.62

* More accurately, 5 minutes

These monomers had the following properties: 2-methyl-1,3-pentadiene, b. p. 75.5°/760 mm, n^{20}_D 1.4455, d^{20}_4 0.7179; 2-ethyl-1,3-butadiene, 66.6°/760 mm, n^{20}_D 1.4328, d^{20}_4 0.7154; 2-isopropyl-1,3-butadiene, b. p. 86-87°, n^{20}_D 1.4318, d^{20}_4 0.7252.

In the polymerization of isoprene to obtain rubber similar to natural rubber, other investigators have used metallic lithium or Ziegler catalyst [5] as the initiator of the process. We also used metallic lithium for the polymerization of the higher dienic hydrocarbons; in part of the experiments, butyllithium was used as the initiator. The polymerizations were carried out in glass ampoules at temperatures of from 50 to 100°. The degree of polymerization was 98-100%.

TABLE 2

Properties of the Alkylbutadiene Polymers

Polymer	Plasticity	Glass transition temp., °C	Properties of the gum rubber vulcanizates		
			tensile, kg/cm²	relative elongation, %	permanent set
Polyisoprene	0.35	− 68	235	1180	14
Polyethylbutadiene	0.56	− 76	200	1220	14
Polyisopropylbutadiene	0.36	− 52	116	1080	16
Polymethylpentadiene	0.66	− 28	200	620	14

As seen from the data presented in Table 1, the polymerizations of 2-ethyl-1,3-butadiene and 2-isopropyl-1,3-butadiene proceeded at satisfactory rates.

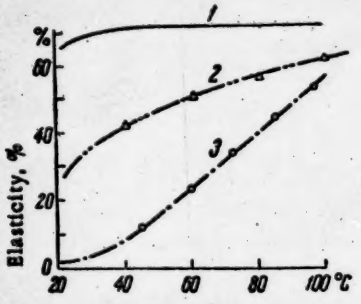


Fig. 1. Rebound resilience of gum rubber vulcanizates. 1) 2-ethyl-1,3-butadiene; 2) 2-isopropyl-1,3-butadiene, 3) 2-methyl-1,3-pentadiene.

The presence of a methyl group in the α-position with respect to a double bond in 2-methyl-1,3-pentadiene led to a sharp retardation in the polymerization process. During polymerization in the presence of butyllithium, the process required 16 hours at 50° and 7 hours at 70°. The polymerization of 2-ethylbutadiene at 70° required for 5 minutes.

The polymers differed considerably from each other with respect to glass transition temperature (Table 2).

The methylpentadiene polymer had a relatively high glass transition temperature; in this polymer, each unit, which is added 1,4, has two methyl groups. Isopropylbutadiene polymer, which has an isopropyl group in each unit, had a lower glass transition temperature. Polyethylbutadiene had the lowest glass transition temperature; it was even lower than the glass transition temperature of natural rubber or polyisoprene.*

With respect to tensile strength of the unreinforced vulcanizates, the ethylbutadiene and methylpentadiene polymers differed little from polyisoprene. However, the methylpentadiene polymer had low elasticity (Fig. 1). Polyethylbutadiene was not inferior to polyisoprene with respect to elasticity.

These investigations have shown that not only polyisoprene, but also polyethylbutadiene rubber has high tensil and high elasticity in the vulcanized state. The latter somewhat excels isoprene rubber with respect to cold resistance.

LITERATURE CITED

[1] A. A. Korotkov, K. B. Piotrovskii, and D. P. Feringer, Proc. Acad. Sci. USSR, Div. Chem. Sci. 110, 89 (1956).**

[2] S. A. Subbotin, V. V. Samoletova, and A. K. Znamenskaia, Chem. Ind. 7, 21 (1956).

* As was previously shown by Marvel et al. [11], a 2-ethyl-1,3-butadiene polymer prepared by emulsion polymerization also had a low glass transition temperature.

** Original Russian pagination. See C. B. Translation.

[3] Rubber Age 76, 4, 588 (1955).

[4] Rubber J. 129, 9, 278 (1955).

[5] Rubber Age 78, 1, 99 (1955).

[6] Iu. A. Gorin, A. A. Vasil'ev, and A. K. Panteleeva, J. Gen. Chem. 17, 917 (1947).

[7] C. S. Marvel, R. L. Myers, and J. H. Saunderers, J. Am. Chem. Soc. 70, 1694 (1948).

[8] J. W. Rephe, Acetylene Chemistry (New York, 1949), p. 10.

[9] C. S. Marvel and L. R. Williams, J. Am. Chem. Soc. 70, 3842 (1948).

[10] Chem. and Eng. News 33, 5026 (1955).

[11] C. S. Marvel, J. L. R. Williams, and H. E. Baumgarten, J. Polymer 4, 583 (1949).

S. V. Lebedev All-Union Synthetic Rubber
Scientific Research Institute

Received March 22, 1958

THE STEREOCHEMISTRY OF σ,π-CONJUGATION

α-CHLOROMERCURICAMPHENILONE

Academician A. N. Nesmeianov and I. I. Kritskaia

At the beginning of 1950, one of us [1] compared a number of factors which decrease (or which cause to be absent) the ability of atoms (or groups) joined to a carbon atom at a bridge end of a bicyclic system to exchange. In October, 1950, a review by Fawcett [2] appeared on this same subject. Here, the inertness was treated from the point of view of Bredt's rule [3] with respect to the impossibility of forming a double bond at a bridge end of a bicyclic system. Actually, a number of cases of inertness of atoms at bridge ends of bicyclic systems are naturally explained by Bredt's rule; among these are, for example, the inability of α-bicyclic ketones to enolize and the impossibility of dehydration or dehydrohalogenation by removal of H, Hal, or OH at a bridge end. A number of other phenomena, such as the impossibility of decarboxylation of a β-keto acid with the carboxyl at the end of a bridge (camphenilonecarboxylic acid, for example, distills without decomposition at 312°, while 1,3,3-trimethylcyclohexanone-2-carboxylic acid decomposes even at room temperature) and the inability of the hydrogens of camphenilone to exchange with deuterium even in the presence of a base [4] (in contradistinction to the monocyclic ketones of similar structure, 2,6,6-trimethylcyclohexanone and 2-methyl-6-spirodecanone)—such cases require special proof that decarboxylation of β-keto acids and deuterium exchange in ketones proceed through an enolization stage. The mechanism of decarboxylation has been given in a paper by Pedersen [5]. The widely studied nonexchangeability of halogen at a bridge end obviously has no relation to Bredt's rule, but has been explained by the necessity of Walden inversion during nucleophilic exchange. But Walden inversion is impossible at the end of a bridge in a bicyclic system. The facts of nonexchangeability at a bridge end, which clearly cannot be explained by either route, impelled one of us, in 1950, to propose that the axes of the σ- and π-electron orbitals must be parallel for complete development of σ,π-conjugation and that perpendicularity of these axes disrupts conjugation [1]. This requirement is analogous to the requirement of planarity in a π,π-conjugated system. The present work provides a measure of confirmation of this hypothesis. In 1956, apparently not knowing of our 1950 article, Corey and Sneen [5a] published an analogous proposal, applying it to the case of enolization of cyclic ketones with different conformations (axial and equatorial) of the α-C—H bonds.

The α-chloromercuricamphenilone synthesized by us had the mercury atom joined to the carbon at the bridge end, which is simultaneously the α-atom with respect to the carbonyl group. A mercury atom connected to the α-carbon atom of open-chain or cyclic ketones and aldehydes is extremely exchangeable, far exceeding in this respect a mercury atom in alkyl compounds. α-Chloromercurioxo compounds are hydrolyzed by water in the presence of KI with replacement of mercury by hydrogen. The same replacement in accomplished by dilute mineral acids in the cold. They are readily triphenylmethylated by triphenylchloromethane, and are readily symmetrized by ammonia to α-mercuribis(oxo-compounds). Their mercury atoms readily undergo isotope exchange both with mercury and with mercuric chloride labeled with radioactive Hg^{203}, as shown by the work of O. A. Reutov and U Ian-tsei [6]. Symmetrical mercuribis (α-oxo compounds) have even greater reactivity.

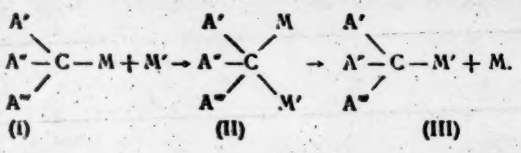
According to the data of Winstein [7], mercury at a bridge end in a compound with no carbonyl group (in 4-mercuribiscamphane), if it is less mobile than in a dialkylmercury, is insignificantly so. Thus, it is replaced by halogen by the action of aqueous solutions of strong mineral acids, or it is replaced by hydrogen on heating with concentrated acetic acid.

4-Chloromercuricamphane is symmetrized by the action of sodium stannite to 4-mercuribiscamphane, and the latter with mercuric chloride readily gives the original chloromercuricamphane. The sum total of these facts

indicates that exchanges of this type proceed without Walden inversion, which is impossible at the end of a bridge. Indeed, direct experiments by one of us, O. A. Reutov and Knol' [8] and by Reutov and co-workers [9] showed that exchange of R'R"R"' HgCl both with Hg^{203} and with $Hg^{203}Br_2$ is accomplished without change of configuration. Consequently, just the fact of the occurrence of mercury at the end of a bridge cannot serve as a reason for its nonexchangeability. Previously, in a paper by one of us and I. F. Lutsenko [10], it was shown that the cause of the mobility of mercury in α-mercurized oxo compounds is not enolization, but is conjugation of the Hg—C and C=O bonds. Moreover, the mercury atom in α-mercuricamphenilone is exceptionally inert, unexpectedly more so even than in Winstein's material. The effect of the α-carbonyl is completely absent. At our request, O. A. Reutov and U Ian-tsei [6] compared the exchangeabilities of mercury in α-chloromercuricamphenilone and α-bromomercuricyclohexanone. In the first case, exchange was not complete under any of the conditions (40 hours, 75-100°), while in the second case, exchange with the metal was 100% after 2 hours at 23°, and exchange with mercuric bromide was also 100% after 2 hours at 50° (acetone). Chloromercuricamphenilone does not react with concentrated hydrochloric acid even when refluxed many hours, the bond of the mercury with carbon is not affected by the usual symmetrizing agents, including KI, and it does not react with $(C_6H_5)_3CCl$. Symmetrization to di-α-camphenilonylmercury can be accomplished with difficulty by heating the corresponding sulfide to 215-220°. The reaction $R_2Hg + HgCl_2 \rightarrow 2RHgCl$ (which proceeds without Walden inversion) does go in our case, though slowly. Reaction with concentrated acetic acid (80°, 13 hours) absolutely does not occur. Reduction of α-chloromercuricamphenilone by $LiAlH_4$ and also reaction with iodine in dioxane proceeds considerably more slowly than with Winstein's compounds. Thus, this exceptional inertness of the system Hg—C—C=O does not depend on the effect of Walden inversion, nor is Bredt's rule an explanation. The only remaining explanation is disruption of the conjugation of the Hg—C and C=O bonds as a result of a perpendicular disposition of the axes of the electron orbitals and the exclusion of the possibility of overlapping of the latter.

Our rule, which was formulated by us in 1950 and which obtains further proof in the present work, is broader than Bredt's rule. But it obviously includes Bredt's rule as a special case. Actually, overlapping of the electron orbitals of two σ- and π-electrons from one of two pairs of σ- and π-bonds of neighboring carbon atoms is possible to the greatest extent when the axis of the σ-bond and the π-orbital are parallel. In this case, the electron of the σ-bond to some degree begins to play the role of a π-electron, binding (permanently or in the transition state) the embryonic π-bond with the π-electron of the neighboring carbon. If, as a result of the nature of the reaction, such an embryonic π-bond must be converted to an actual π-bond, Bredt's rule comes into force.

The unexpectedly high inertness of the mercury in α-chloromercuricamphenilone, in comparison with Winstein's compounds, also requires an explanation. It is possible to conceive of the transition complex as having configuration (II) in substitution reactions (homolytic and electrophilic) which occur without Walden inversion. The valence angles ACA must be less in (II) than in (I) or (III), and this must lead to an increase in the energy of activation during replacement of an atom at a bridge end in a bicyclic system with its rigid structure,



with its decreased, in comparison to 109°, value of the C—C"—C valence angles, and with the small possibility of a further decrease in the angles. Such an increase in activation energy will be still greater if the bicyclic system, in place of a tetrahedral carbon atom with its natural valence angle of 109°, includes a carbonyl carbon with its natural valence angle of 120°, the angles being reduced to less than 109°. Further reduction in this case, with the deviation being not from 109°, but from 120°, must sharply increase the activation energy of the activated state. If such an argument is correct, then substitution of hydrogen for the carbonyl oxygen in α-mercurized camphenilone must increase the mobility of the mercury to the degree inherent in Winstein's materials. On the contrary, replacement of the O by CH_2 with the formation of the group $C=CH_2$ cannot change the lack of mobility of the mercury.

EXPERIMENTAL

Since mercurization of camphenilone does not proceed under any conditions, and the corresponding halogen derivative is unreactive, we used for our purpose the method involving decomposition of organic peroxides in the presence of mercury or mercury salts of carboxylic acids, a reaction developed by Razuvaev and co-workers [11].

Camphenonoyl peroxide was prepared by prolonged agitation of an ethereal solution of the anhydride of camphenonic acid (m. p. 31°) [1] with an alkaline solution of 10% hydrogen peroxide. The ether layer was repeatedly extracted with a 5% solution of sodium bicarbonate. The yield of peroxide was 22%, decomposition temperature 110-112°. Iodometric titration showed 91% active oxygen.

Found %: C 66.46, 66.45; H 7.29, 7.39. $C_{20}H_{26}O_6$. Calculated %: C 66.28; H 7.23.

Decomposition of the camphenonoyl peroxide in the presence of finely dispersed metallic mercury in boiling benzene gave only α-phenylcamphenone, which steam-distilled as a crystalline material with a m. p. of 56-57° (from alcohol).

Found %: C 83.93, 83.72; H 8.52, 8.56. $C_{15}H_{18}O$. Calculated %: C 84.05; H 8.46.

The reaction of camphenonoyl peroxide with the mercury salt of camphenonic acid was successful; this reaction was carried out in the melt, without a solvent. 2 g of the mercury salt and 1.5 g of the peroxide were carefully mixed and cautiously heated with rapid stirring to 70-80°. The reaction gradually became vigorous and then explosive, and a significant amount of metallic mercury was liberated. After the explosion, the reaction mixture was heated for another 30 minutes, and then to the cooled reaction mixture was added an excess of an aqueous-acetone solution of potassium chloride. The mixture was stirred for 3-4 hours, allowed to stand overnight, and then steam distilled. α-Bicamphenonoyl – a white, crystalline substance with a characteristic terpene odor – was found in the distillate. The plates melted at 85-86° (from alcohol).

Found %: C 78.40, 78.52; H 9.33, 9.47. $C_{18}H_{26}O_2$. Calculated %: C 78.79; H 9.55.

In addition, an unknown material with a m. p. of 122-123° distilled along with the steam. A large amount of tar remained in the distillation flask, and from the aqueous portion was extracted, with ether, 1.4 g of a mixture of camphenonic acid (1.2 g) and α-chloromercuricamphenilone (from 0.2 to 0.4 g). These substances were fractionally crystallized from alcohol. α-Chloromercuricamphenilone is a readily crystallizable, white material, somewhat soluble in water, readily soluble in the majority of organic solvents, and insoluble in petroleum ether; m. p. 134-136°.

Found %: C 29.01, 29.01; H 3.46, 3.61; Hg 53.35, 53.34; Cl 9.23, 9.27. $C_9H_{13}HgClO$. Calculated %: C 28.96; H 3.51; Hg 53.74; Cl 9.49.

Acid hydrolysis of the chloromercuricamphenilone did not take place at all when the compound was refluxed with concentrated hydrochloric acid for 3 hours or when treated with the acid at room temperature for several days. The original product was recovered; reaction with H_2S gave only a white, acicular precipitate of the sulfide with a decomposition temperature of 212-214° (from alcohol).

Found %: C 30.65, 30.77; H 3.74, 3.85. $C_{18}H_{26}Hg_2SO_2$. Calculated %: C 30.56; H 3.70.

In contradistinction to α-chloromercuriacetone and its homologs, α-chloromercuricamphenilone did not react with potassium iodide in aqueous solution to give an alkali, but did give iodomercuricamphenilone in the form of needles with a m. p. of 134-135° (from alcohol). It decomposed on standing in the light.

Found %: C 23.54, 23.60; H 2.88, 2.86. $C_9H_{13}HgIO$. Calculated %: C 23.26; H 2.82.

In an attempt at symmetrization with sodium stannite at room temperature, we isolated a low-melting product having acid properties; in all probability, opening of the ring occurred under the action of the alkali.

When chloromercuricamphenilone was treated by heating with an aqueous solution of sodium thiosulfate, the above-described sulfide with a decomposition temperature of 212-214° was obtained. When this was heated at 215-220° for 15 minutes, the resulting black mass extracted with acetone, and the extract refluxed with activated carbon, needles of di-2-camphenilonylmercury, m. p. 112-114° (from aqueous alcohol), were obtained in a yield of 80% of theoretical.

Found %: C 45.77, 45.60; H 5.35, 5.33; Hg 42.39, 41.80. $C_{13}H_{20}O_2Hg$. Calculated %: C 45.52; H 5.52; Hg 42.23.

Reaction with $HgCl_2$ in absolute ether for 16 hours, the reverse of symmetrization, gave chloromercuricamphenilone in 50% yield.

When di-α-camphenilonylmercury was heated to boiling with concentrated HCl for 30 minutes, α-chloromercuricamphenilone was obtained in 88% yield; m. p. 131°.

Reduction of α-chloromercuricamphenilone with excess $LiAlH_4$ in ether solution at room temperature for 65 hours gave 72% of α-bromomercuricamphenilone (LiBr was present in the reaction mixture), m. p. 158°, and about 10% of camphenilol, m. p. 84-86° [13].

Found %: C 25.67, 25.99; H 3.40, 3.38; Br 18.69, 18.97; Hg 47.72, 47.82. $C_9H_{13}OHgBr$. Calculated %: C 25.89; H 3.13; Br 19.14; Hg 48.0.

The reaction of iodomercuricamphenilone with iodine in absolute, peroxide-free dioxane was carried out in a stream of pure nitrogen. The system was evacuated to 0.5 mm, and then filled with nitrogen. After eight such cycles, the solutions of iodine and iodomercuricamphenilone were mixed at room temperature. There was absolutely no decoloration. After 45 hours, the amount of iodine in the reaction mixture was determined by titration. It was found that 30% of the iodine originally present had reacted.

LITERATURE CITED

[1] A. N. Nesmeianov, Scientific Records Moscow State Univ. No. 132 (1950).

[2] F. S. Fawcett, Chem. Revs. 47 (1950).

[3] J. Bredt, Lieb. Ann. 437, 1 (1924).

[4] A. N. Nesmeianov, D. N. Kursanov, K. A. Pecherskaia, and Z. N. Parnes, Bull. Acad. Sci. USSR, Div. Chem. Sci. (1949), p. 592.

[5] K. J. Pedersen, J. Phys. Chem. 58, 243 (1936).

[5a] E. J. Correy and R. A. Sneen, J. Am. Chem. Soc. 78, 6269 (1956).

[6] O. A. Reutov and U Ian-tsei, Proc. Acad. Sci. USSR, Div. Chem. Sci. 117, 1003 (1957). •

[7] S. Winstein and T. G. Traylor, J. Am. Chem. Soc. 78, 2597 (1956).

[8] A. N. Nesmeianov, O. A. Reutov, and P. Knol', Proc. Acad. Sci. USSR, Div. Chem. Sci. 118, 99 (1958).•

[9] O. A. Reutov, Bull. Moscow State Univ. 4, 223 (1957).

[10] A. N. Nesmeianov and L. F. Lutsenko, Proc. Acad. Sci. USSR 59, 707 (1948).

[11] G. A. Razuvaev, Iu. A. Ol'dekop, and N. A. Meier, J. Gen. Chem. 25, 697 (1955).•

[12] G. Komppa and A. Klami, Ber. 68, 2001 (1935).

[13] W. Jagelki, Ber. 32, 1503 (1899).

Institute of Heteroorganic Compounds
Academy of Sciences USSR

Received April 21, 1958

• Original Russian pagination. See C. B. Translation.

SYNTHESIS OF DERIVATIVES OF 5-MERCAPTOINDOLE AND 5-MERCAPTO-1-METHYLINDOLE

Corresponding Member AN SSSR A. P. Terent'ev

and M. N. Preobrazhenskaia

In connection with the high physiological activity of various indole compounds containing a hydroxy (or alkoxy) group in the benzene ring (serotonin, alkaloids, reserpine, eserpine, etc.), the synthesis and study of the chemical properties and of the physiological activity of various derivatives of 5-mercaptoindole appeared to be of interest. Up to the present, no substituted indoles containing a divalent sulfur atom in the 4, 5, 6, or 7 position has been described. Indeed, it is very difficult to prepare indoles substituted in the benzene ring by means of the Fischer method, the Reissert method, or any of the other methods used for the synthesis of such compounds.

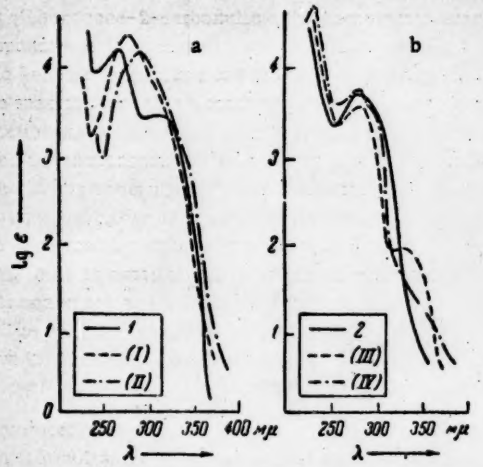
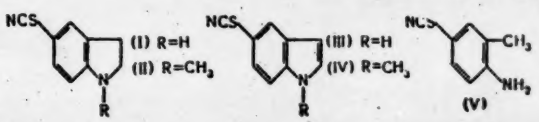


Fig. 1. Ultraviolet spectra of indolines (a) and indoles (b). 1) 5-bromo-1-methylindole.

Application of the new route developed by us for the synthesis of indoles substituted in the benzene ring [1] permitted preparation of a number of derivatives of 5-mercaptoindole and 5-mercapto-1-methylindole. The synthesis was carried out as follows. The indole (or 1-methylindole) was reduced to the corresponding dihydroindole (indoline). Indoline, like other aromatic amines, enters into thiocyanation reactions. The resulting thiocyanoindoline was dehydrogenated with the formation of the thiocyanoindole.

5-Thiocyanoindoline (I), 5-thiocyano-1-methylindoline (II), 5-thiocyanoindole (III), and 5-thiocyano-1-methylindole (IV) were prepared by this method.



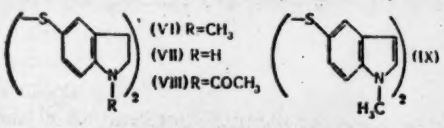
The yield of (III) was 57% calculated on the original indole; the yield of (IV) was 34%.

The thiocyano group entered the 5-position of the indoline ring, which is similar to the thiocyanation of o-toluidine in which 5-thiocyano-o-toluidine is formed [2]. During bromination of indolines also, a hydrogen atom attached to the number 5 carbon atom is replaced. 5-Bromo-1-methylindoline, which was dehydrogenated into 5-bromo-1-methylindole, was prepared by bromination of 1-methylindoline. Oxidation of the 5-bromo-1-methylindole with chromic acid gave 5-bromo-1-methylisatin, which corresponded to 5-bromo-1-methylisatin synthesized from isatin.

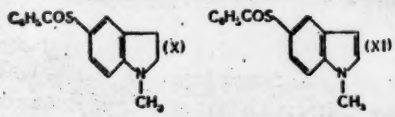
It is interesting to note that the absorption spectra in the ultraviolet region of 5-bromo-1-methylindoline and the thiocyanoindolines are dissimilar, while the absorption spectra of (III) and (IV) are similar to the spectrum

of 5-bromo-1-methylindole* (see Fig. 1).

The thiocyano compounds form disulfides when refluxed with alkali. This route was used to prepare from (II) the corresponding disulfide (VI). The disulfide (VII), which is not substituted at the nitrogen atom, could be isolated only in the form of its diacetyl derivative (VIII). 5,5-Bis(1-methylindolyl) disulfide (IX) was prepared from (IV).



By reduction and subsequent benzoylation of (II), 5-benzoylmercapto-1-methylindoline (X) was synthesized, dehydrogenation of which, with chloranil in xylene, gave 5-benzoylmercapto-1-methylindole (XI).



Work with these compounds requires a number of safeguards, since they cause severe dermatitis, which appears 2-3 weeks after exposure.

EXPERIMENTAL

5-Thiocyanoindoline (I). 40 g of potassium thiocyanate was added to a solution of 11.9 g of indoline in 50 ml of methyl alcohol, and to the resulting reaction mixture, cooled to below 0°, was added dropwise and with stirring a solution of 16 g of bromine in 20 ml of methyl alcohol saturated with sodium bromide. When all of the solution had been added, the reaction mixture was poured into an aqueous solution of soda (500 ml). An oil separated, and it crystallized after several minutes. The yield was 17.1 g (97%). M. p. 64.5-65° (from methyl alcohol).

Found %: C 61.46; H 4.53. $C_9H_8N_2S$. Calculated %: C 61.33; H 4.58.

U. v. spectrum of (I): λ_{max} = 272 mμ; log ϵ_{max} = 4.38.

0.6 g of (I) was dissolved in 50 ml of acetic anhydride and heated to boiling for 15 minutes; the solution was poured into water. 0.6 g of crystalline 1-acetyl-5-thiocyanoindoline was obtained. M. p. 102.5-103.5° (from heptane).

Found %: C 60.32; H 4.59; S 14.54. $C_{11}H_{10}ON_2S$. Calculated %: C 60.52; H 4.62; S 14.69.

5-Thiocyano-1-methylindoline (II). The preparation of (II) was carried out under the same conditions used for the preparation of (I). 13.3 g of methylindoline was thiocyanated. After addition of the bromine solution was complete, the reaction mixture was poured onto ice. An oil was obtained, which crystallized after several hours.**

The crystals were filtered, and extraction of the mother liquor with ether gave an additional several grams of 5-thiocyano-1-methylindoline. The total yield was 15.9 g (84%). 13 g of (II) were obtained after recrystallization from methyl alcohol. M. p. 45-45.5°.

* The spectra were taken with an SF-4 spectrophotometer. The solvent was methyl alcohol.

** It was usually necessary to introduce a seed crystal in order to crystallize the oil. A small amount of crystalline (II) was prepared by distilling 2-3 g of the material under vacuum. 5-Thiocyano-1-methylindoline comes over, with decomposition, at a temperature above 150° at 2 mm Hg; however, the red liquid which distills readily crystallizes. Vacuum distillation of a larger amount cannot be accomplished (complete decomposition occurs prior to distillation).

Found %: C 63.20; H 5.14. $C_{10}H_{10}N_2S$. Calculated %: C 63.11; H 5.30.

U. v. absorption spectrum of (II): λ_{max} = 286 mμ; log ϵ_{max} = 4.16.

5-Thiocyanoindole (III). A solution of 4.1 g of 5-thiocyanoindoline and 5.7 g of chloranil in xylene (100 ml) was heated to boiling over a period of 2 hours. After cooling the reaction mixture, it was agitated several times with aqueous alkali (20%), and the xylene solution was filtered and washed successively with water, hydrochloric acid (1:1), and again with water. After distillation of the xylene under vacuum, 2.8 g of 5-thiocyanoindole (68%) was obtained. M. p. 104-105° (from heptane).

Found %: C 62.16; H 3.46. $C_9H_6N_2S$. Calculated %: C 62.04; H 3.47.

U. v. absorption spectrum of (III): λ_{max} = 282 mμ; log ϵ_{max} = 3.66; λ_{max} = 330 mμ; log ϵ_{max} = 2.04.

5-Thiocyano-1-methylindole (IV). 4.8 g of 5-thiocyano-1-methylindoline and 6.2 g of chloranil in 100 ml of xylene were heated to boiling over a period of 20 minutes. After cooling, the solution was agitated several times with 20% alkali, filtered, washed successively with water, hydrochloric acid (1:1), and water; the xylene was distilled under vacuum, and the residual oil was distilled. The material came over at a temperature of 160-180° at 2 mm Hg. The red oily liquid rapidly crystallized; the yield was 2.4 g (51%). M. p. 57-57.5° (from heptane).

Found %: C 63.69; H 4.36. $C_{10}H_8N_2S$. Calculated %: C 63.78; H 4.28.

U. v. absorption spectrum of (IV): λ_{max} = 235 mμ; log ϵ_{max} = 4.72; λ_{max} = 288 mμ; log ϵ_{max} = 3.74. We note that a mixed sample with 5-thiocyano-1-methylindoline showed no depression of the melting point. The m. p. of the mixture of (II) and (IV) (1:1) was 46-47°.

1,1-Dimethyl-5,5-diindolinyl disulfide [5,5-bis(1-methylindolyl) disulfide] (VI). A suspension of 1.9 g of (II) in 100 ml of concentrated alkali was heated to boiling for 6 hours, and the oil which separated was extracted with ether. After evaporation of the ether, 1 g of disulfide (VI) was obtained. The material was purified for analysis by solution in dilute hydrochloric acid, subsequent precipitation with sodium bicarbonate, and recrystallization from acetone. The material was in the form of bright yellow crystals. M. p. 96.5-98°.

Found %: C 65.88; H 6.06. $C_{18}H_{20}N_2S_2$. Calculated %: C 65.81; H 6.14.

U. v. absorption spectra: λ_{max} = 268 mμ; log ϵ_{max} = 4.18; λ_{max} = 312 mμ; log ϵ_{max} = 4.19. In a similar manner, starting with 5-thiocyano-1-methylindole, was prepared 1,1-dimethyl-5,5-diindolyl disulfide (IX). M. p. 101-102° (from heptane).

5,5-Bisindolinyl disulfide (VIII). This compound was obtained in the form of an oil by refluxing 5-thiocyanoindoline with concentrated alkali. Heating the disulfide with acetic anhydride gave the crystalline diacetyl derivative (1,1-diacetyl-5,5-diindolinyl disulfide) (VIII). M. p. 201-203° (from octane).

Found %: C 62.56; H 5.20. $C_{20}H_{20}O_2N_2S_2$. Calculated %: C 62.47; H 5.25.

5-Benzoylmercapto-1-methylindoline (X). 5.1 g of (II) was dissolved in 100 ml of concentrated hydrochloric acid, 10 g of metallic tin was added, and the mixture was heated on a boiling water bath. The reaction mixture at first turned red, and then decolorized gradually. Cooling of the reaction mixture caused a viscous oil to separate (apparently a tin complex of 5-mercapto-1-methylindoline). The oil was dissolved in acetone, precipitated with water, and extracted with chloroform. Benzene, benzoyl chloride, and aqueous alkali were added to the viscous, reddish mass resulting from evaporation of the solvent, and the reaction mixture was agitated for 30 minutes. The benzene layer was separated, washed with water, and the benzene was distilled under vacuum. 2.8 g (33%) of 5-benzoylmercapto-1-methylindoline was obtained. The material was in the form of yellow crystals. M. p. 104-106.5° (from isooctane). The material was purified for analysis as follows: it was dissolved in dilute hydrochloric acid; the hydrochloric acid solution was filtered, washed with benzene, and neutralized with sodium bicarbonate; the precipitated crystals were recrystallized several times from isooctane. M. p. 105.5-106.5°.

Found %: C 71.43; H 5.63. $C_{16}H_{15}ONS$. Calculated %: C 71.33; H 5.61.

U. v. absorption spectrum of (X): λ_{max} = 239 mμ; log ϵ_{max} = 4.06; λ_{max} = 275 mμ; log ϵ_{max} = 4.37.

5-Benzoylmercapto-1-methylindole (XI). A solution of 1.8 g of (X) and 1.64 g of chloranil in xylene was refluxed for 15 minutes, and, after cooling, was washed successively with 20% alkali, water, dilute hydrochloric acid, and water. After distillation of the solvent under vacuum, an oily liquid was obtained, which crystallized upon the addition of heptane. 1.1 g (61%) of a dark, crystalline material was obtained. The material was easily purified by boiling in heptane solution with carbon. The material was in the form of colorless crystals. M. p. 118.5-119.5°.

Found %: C 71.72; H 5.14; N 5.06. $C_{16}H_{13}ONS$. Calculated %: C 71.86; H 4.90; N 5.25.

U. v. absorption spectrum: $\lambda_{max} = 237$ mμ; log $\epsilon_{max} = 4.70$; $\lambda_{max} = 276$ mμ; log $\epsilon_{max} = 4.03$.

LITERATURE CITED

[1] A. P. Terent'ev and M. N. Preobrazhenskaia, Proc. Acad. Sci. USSR, Div. Chem. Sci. 118, 302 (1958).*

[2] S. A. Zaboev and N. A. Kudriavtsev, J. Gen. Chem. 5, 1607 (1935).

M. V. Lomonosov Moscow State University

Received March 19, 1958

* Original Russian pagination. See C. B. Translation.

DEHYDROGENATION OF n-PENTANE AND ISOPENTANE IN THE PRESENCE OF CHROME-ALUMINA-POTASSIA CATALYST

Corresponding Member AN SSSR N. I. Shuikin,
E. A. Timofeeva, and T. P. Dobrynina

We have previously shown that a chrome-alumina-potassia catalyst of the composition $Cr_2O_3 + Al_2O_3 + K_2O$ (5.6 : 90.7 : 3.7 mole %) readily catalyzes the dehydrogenation of n-pentane and isopentane [1-3].

Indications of the use of a similar type of mixed catalysts for the dehydrogenation of lower alkanes are found in the works of earlier authors [4, 5]. However, in a series of experiments we found: a) the most favorable ratios of catalyst components and b) the conditions required for preliminary catalyst activation.

The catalyst was first heated in a stream of air to the required temperature. After purging the air from the catalyst with nitrogen, the catalyst was treated with hydrogen for 1.5 hours. Preliminary treatment of the catalyst with pentane or isopentane has the same activating effect. The amount of hydrocarbon required for this purpose depends on the conditions under which the experiment is to be carried out, the temperature and the space rate. Activation of the catalyst is complete when evolution of CO and CO_2 stops while hydrocarbon is being passed through the catalyst. Regeneration of the spent catalyst was carried out by heating in a stream of air at 680-700°, as a rule, for 5 hours. Reproducibility of the catalyst activity was good. Catalyst activity was maintained at a high level for over 200 hours by periodic regeneration.

TABLE 1

Product Distribution With Respect to Temperature (in mole percent of hydrocarbon fed).

Temp. °C	Unreacted hydrocarbon	Alkenes	Isoprene	Amt. of hydrocarbon converted to "coke"	Amt. of hydrocarbon converted to gas	Balance
			n-Pentane			
500	61	32	—	4	2	99
527	48	38	—	10	6	102
550	36	42	—	13	10	101
			Isopentane			
500	55	39	2	2	2	100
527	42	46	2	6	3	99
550	32	47	5	9	6	99

The effect of temperature, space rate, and process cycle length on the dehydrogenation activity of chrome-alumina-potassia catalyst was studied in the present work. In all experiments, the amount of catalyst was 30 ml and the inside diameter of the catalyst tube was 18 mm. The dimensions of the catalyst grains were approximately 3·3·3 mm. After each regeneration and before the next experiment, the catalyst was treated with hydrogen for 1.5 hours. The hydrocarbons were automatically fed by means of a syringe buret. The temperature was measured with a thermocouple located in the catalyst bed. The receiver was cooled with solid

carbon dioxide. 10 ml of hydrocarbon was used in each experiment. The olefin contents of the catalyzates were determined by a bromometric method [6, 7], and the isoprene contents were determined gravimetrically by reaction with maleic anhydride.

TABLE 2

Dependence of Yields of Pentenes and Isopentenes on Space Rate

Temp. °C	Space rate, hours^{-1}	Yield, mole % of hydrocarbon fed	
		pentenes	isopentenes
500	0,5	31	38
	0,8	25	33
	1,1	19	27
527	0,3	38	—
	0,5	39	45
	0,8	32	44
	1,1	30	42
550	0,3	40	44
	0,5	41	46
	0,8	—	45
	1,1	39	45
575	0,3	—	35
	0,5	—	37
	1,1	—	37

Effect of temperature. The experiments were carried out at 450-575° and a space rate of 0.5 hours^{-1}. The process period was one hour. The catalyzate and gas were collected during the last 43-44 minutes. Table 1 presents the results of experiments carried out at temperatures such that equilibrium yields of pentenes and isopentenes were obtained.

Effect of space rate. The results, presented in Table 2, show that at space rates in the range of 0.3 to 1.1 hours^{-1}, the yields of pentenes and isopentenes depend on the temperature, it being lower the more marked this effect. Thus, a change in space rate from 0.5 to 1.1 hours^{-1} at 500° led to a decrease in isopentene yield from 38 to 27% and a decrease in pentene yield from 31 to 19%. The same change in space rate at 527° led to a decrease in isopentene yield from 45 to 42% and a decrease in pentene yield from 39 to 30%. An increase in space rate within the range of 0.3 to 1.1 hours^{-1} at 550 and 575° had practically no effect on pentene and isopentene yields. The isoprene yield was almost independent of space rate, and varied from 1-2% at 500° to 5-6% at 550°.

Effect of process cycle length without regeneration. The dehydrogenation of isopentane at 500, 527, and 550° and a space rate of 1.1 hours^{-1} was investigated in this series of experiments. At each of these temperatures, 28 experiments were carried out without catalyst regeneration. It was shown that the higher the temperature, the more rapidly the catalyst activity decreases with time, as can be seen from Fig. 1. The isopentene content of catalyzates obtained at 18 minutes of process cycle increased with an increase in temperature from 25 weight% of the isopentene fed at 500° to 45 wt. % at 550°. However, the isopentene yield after a process period of 3 hours and 18 minutes was somewhat higher at 527° than at 550°, namely, 39.6 against 37.1%. The isopentene yield in catalyzates obtained after a process period of 8 hours and 24 minutes at 527° (30%) was also higher than at 550° (26%). Thus, at 550°, it is expedient to carry out the reaction in short cycles, not more than 1 hour, and at high space rates. This requires frequent regeneration of the catalyst. At 527°, the dehydrogenation of isopentene can be carried out in longer cycles, longer than 3 hours. Carrying out the reaction at 500° is apparently less expedient owing to the comparatively low isopentene yields at the start of the period. However, the process period can be longer at this temperature.

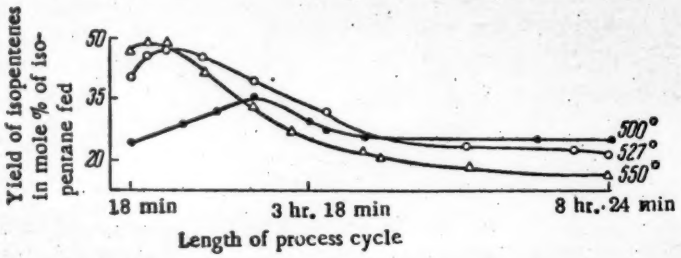


Fig. 1. Variation in isopentene yield with length of the process cycle at various temperatures.

By way of example, we cite the basic data obtained when the process was carried out at 527°, a space rate of 1.1 hours^{-1}, and a process period length of 3 hours and 18 minutes. Under these conditions, the catalyzate

contained 44 wt.% isopentenes and 2.6 wt.% isoprene. Recalculated on the basis of the isopentene fed, these values are 40 and 2%, respectively, and on the basis of the isopentene consumed, they become 78 and 5%, respectively. The productivity of the process with respect to isopentenes was 274 g/liter·hour and with respect to isoprene, 16 g/liter·hour.

LITERATURE CITED

[1] N. I. Shuikin, T. P. Dobrynina, E. A. Timofeeva, and Iu. P. Egorov, Bull. Acad. Sci. USSR, Div. Chem. Sci. (1955), 952. •

[2] N. I. Chouikine, T. P. Dobrynina, and E. A. Timofeeva, Rev. Inst. Franc. du Petrole 11, 1185 (1956).

[3] N. I. Shuikin, E. A. Timofeeva, and V. M. Kleimenova, Bull. Acad. Sci. USSR, Div. Chem. Sci. (1957), 875.•

[4] J. Burgin, H. Groll, and R. M. Roberts. Nat. Petrol. News 30, R-432 (1938).

[5] A. V. Grosse and V. N. Ipatieff, Ind. and Eng. Chem. 32, 268 (1940).

[6] G. D. Gal'pern, Trans. Inst. Petr. Acad. Sci. USSR 4 (1954).

[7] E. A. Timofeeva, V. M. Kleimenova, and T. P. Dobrynina, Bull. Acad. Sci. USSR, Div. Chem. Sci. (1957), 122.•

N. D. Zelinskii Institute of Organic Chemistry
Academy of Sciences, USSR

Received January 4, 1958

• Original Russian pagination. See C. B. Translation.

ON THE STRUCTURE OF THE PRODUCTS OF THE REACTION OF SOME α-HALOKETONES OF THE CARBOCYCLIC SERIES WITH TRIETHYL PHOSPHITE AND WITH SODIUM DIETHYL PHOSPHITE

Academician B. A. Arbuzov, V. S. Vinogradova, and N. A. Polezhaeva

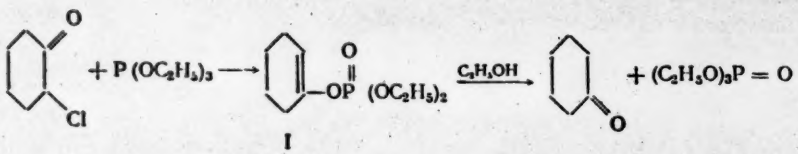
Over the past few years, we have undertaken the study of esters of β-ketophosphonic acids [1]. The original aim of the investigation was to detect the presence of keto-enol tautomerism in esters of β-ketophosphonic acids.

It was found, however, that the A. E. Arbuzov rearrangement involving triethyl phosphite and α-haloketones, which was used to prepare the β-ketophosphonic acid esters, proceeds in a complex manner, and that along with the expected β-ketophosphonic acid esters, mixed esters of phosphoric acid were obtained [2]; this complicated the investigation of the β-ketophosphonic acid esters, and it also explained certain deviations which we had observed in the chemical and physical properties of the β-ketophosphonic acid esters [3].

Our investigations showed that in the case of the reaction of sodium diethyl phosphite with α-haloketones, the Michaelis-Becker reaction also proceeds in a complex manner and leads to the formation of esters of epoxyphosphonic acids [4] along with the esters of β-ketophosphonic acids.

In the present communication, we present data obtained by us on the structures of the products of the interaction of triethyl phosphite or of sodium diethyl phosphite with α-chlorocyclohexanone, α-chloro-α-methylcyclohexanone, and an ester of pyroracemic acid.

In 1955, A. N. Pudovik [5] showed that the product of the action of triethylphosphite on α-chlorocyclohexanone is a mixed ester of phosphoric acid (I) containing an ester radical having the form of the enol form of cyclohexanone. On transesterification with ethyl alcohol, this ester gave triethyl phosphate and cyclohexanone.



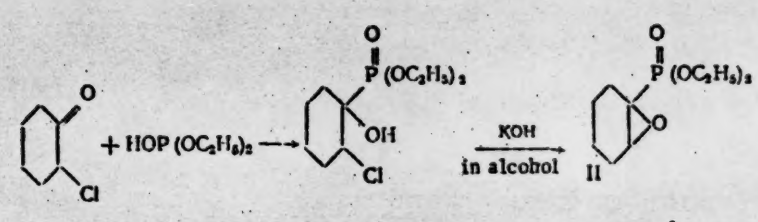
I

To the product of the interaction of α-chlorocyclohexanone with diethyl sodium phosphite he assigned the structure of the diethyl ester of α-phosphonocyclohexanone. We carried out an investigation of the products of the interaction of α-bromocyclohexanone with triethyl phosphite, and it was shown that in this case the product is the mixed ester of phosphoric acid (I), and this was confirmed both by chemical evidence and by Raman spectra.

The study of the product of the interaction of α-chlorocyclohexanone with diethyl sodium phosphite showed that it is neither an unsaturated ester of phosphoric acid nor an ester of phosphonocyclohexanone. On transesterification with ethyl alcohol, it was recovered unchanged. It did not give a dinitrophenylhydrazone with 2,4-dinitrophenylhydrazine. Its Raman spectrum did not contain the carbonyl group frequency. All of these

data indicated that this product has the structure of the diethyl ester of epoxycyclohexanephosphonic acid (II).

This proposed structure was confirmed by synthesizing ester (II) according to the following scheme [4]:



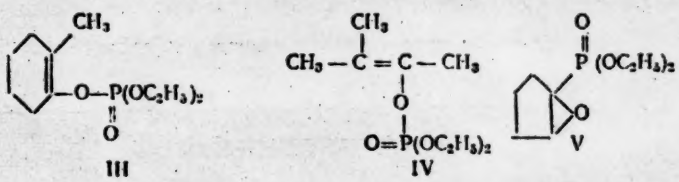
The epoxycyclohexanephosphonic acid ester had the following constants: b. p. 112-114°/2.5 mm, n^{20}_D 1.4571, d^{20}_4 1.1193, MR_D 57.01; these are close to the values of the constants of the product obtained from the Michaelis-Becker reaction. The Raman spectra of the two products were in complete agreement.

Thus, as in the case of aliphatic α-haloketones [4], the product of the action of diethyl sodium phosphite on α-chlorocyclohexanone was shown to be an ester of epoxycyclohexanephosphonic acid, and not an α-phosphonocyclohexanone.

It developed, somewhat unexpectedly, that in the case of α-chloro-α-methylcyclohexanone, the products of the reactions with triethyl phosphite and with diethyl sodium phosphite had closely similar constants and Raman spectra.

On transesterification with ethyl alcohol, both preparations gave triethyl phosphate and methylcyclohexanone, and were thus shown to be the methylcyclohexenyl diethyl ester of phosphoric acid (III); thus, in this case the Arbuzov rearrangement and the Michaelis-Becker reaction lead to the same unsaturated ester of phosphoric acid.

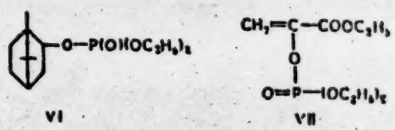
It is interesting to note that, as we have shown in another case – the case of methyl-α-bromoisopropylketone [3-bromo-3-methyl-2-butanone] where there is a halogen at the tertiary carbon – the rearrangement and the Michaelis-Becker reaction lead to the same product – an unsaturated ester of a phosphonic acid (IV) – as was shown by transesterification with ethyl alcohol, which gave methyl isopropyl ketone and triethyl phosphate, and by the Raman spectra.



The product previously obtained by us by the interaction of α-chlorocyclopentanone with diethyl sodium phosphite, as further investigation showed, was an ester of epoxycyclopentanephosphonic acid (V). It did not give a 2,4-dinitrophenylhydrazone, nor did it undergo transesterification with ethyl alcohol. The Raman spectrum did not contain the frequencies associated with the carbonyl group or the C=C bond.

An additional study of the product of the action of diethyl sodium phosphite on α-bromocamphor showed that it is a mixed unsaturated ester of phosphoric acid (VI). On transesterification with ethyl alcohol, it gave camphor and triethyl phosphate.

The product previously obtained by us by the action of diethyl sodium phosphite on bromopyroracemic acid ester proved to be an unsaturated ester of phosphoric acid (VII).



The material presented in the present communication shows the complex course of the reaction between haloketones and diethyl sodium phosphite, which leads to the formation of unsaturated esters of phosphoric acid, esters of epoxyphosphonic acids, and, in some cases, esters of β-ketophosphonic acids [4] depending on the nature of the halide, the reaction conditions, and the alkyl radical substituents.

LITERATURE CITED

[1] B. A. Arbuzov and V. S. Vinogradova, Proc. Acad. Sci. USSR 99, 85 (1954); Bull. Acad. Sci. USSR, Div. Chem. Sci. 54, 284 (1957). *

[2] W. Perkow, Chem. Ber. 87, 755 (1954); A. N. Pudovik and N. M. Lebedeva, Proc. Acad. Sci. USSR 101, 889 (1955); J. F. Allen and O. H. Johnson, J. Am. Chem. Soc. 77, 2871 (1955).

[3] B. A. Arbuzov and V. S. Vinogradova, Proc. Acad. Sci. USSR 106, 263, 465 (1956). *

[4] B. A. Arbuzov, V. S. Vinogradova, and N. A. Polezhaeva, Proc. Acad. Sci. USSR 111, 107 (1956). *

[5] A. N. Pudovik, J. Gen. Chem. 25, 2173 (1955). *

A. M. Butlerov Chemical Scientific-Research Institute
of the V. I. Ulianov (Lenin) Kazan State University

Received January 13, 1958

* Original Russian pagination. See C. B. Translation.

INVESTIGATION OF THE GRAFT COPOLYMERIZATION OF VINYL CHLORIDE WITH DERIVATIVES OF THE METHACRYLIC SERIES

A. A. Berlin, L. V. Stupen', B. I. Fedoseeva, and D. M. Ianovskii

(Presented by Academician N. N. Semenov, April 3, 1958)

During the polymerization of a monomer in the presence of polymeric substances, the latter are subjected to the action of radicals which may be the growing chains or which may derive from the initiator. During this process, as a result of chain transfer, active centers can arise on the macromolecules, and these centers can initiate polymerization of the monomer, which results in the formation of high-molecular-weight compounds of branched or three-dimensional structure. If the chemical nature of the side branching differs from that of the main chain, then graft copolymers are formed which combine the properties of the polymers involved.

The synthesis of graft copolymers by the reaction of polymers with monomers has been developed and has attained technical significance since 1946-1947 [1, 2].

In more recent papers, methods have been described for graft copolymerization based on the use of ionizing radiation and the reaction of functional groups of the macromolecules with monomeric or polymeric substances [3-6].

Below are presented experimental data obtained during the synthesis and investigation of graft copolymers prepared by polymerization of vinyl chloride in a latex of a butyl methacrylate – methacrylic acid copolymer (BMR) and also of graft copolymers prepared by polymerizing a mixture of butyl methacrylate and methacrylic acid in a latex of polyvinyl chloride (PVC).

TABLE 1

Polymer	Cl, %	Polymer analysis [η]	K'	f
Graft of VC on BMR (1:2)	21.7	0.820	0.441	0.668
Control PVC	56.0	0.402	0.331	–
Control BMR-5	–	0.90	0.159	–
Mechanical mixture PVC + BMR-5 (1:2)	18.8	0.69	0.165	–

The polymerization of vinyl chloride in a BMR latex was carried out in an autoclave, in the presence of ammonium persulfate, at a temperature of 45-60°, and at various reagent ratios. CCl_4 and CHI_3 were used as modifiers. The resulting copolymers were reprecipitated three times from cyclohexane solution using methyl alcohol as the precipitant; they were then extracted with acetone to remove the unreacted BMR, and were dried to constant weight. The combined chlorine, the degree of interaction of the monomer with the polymer (f), the intrinsic viscosity, and Huggins' constant of the copolymers were determined. Turbidimetric titration was carried out on the copolymer solution in order to prove that graft copolymer had been formed [7].

Similar determinations were carried out on the BMR, PVC, and the mechanical mixture of these polymers.

As seen from Table 1, Huggins' constant was higher for the graft copolymers than for the linear, control polymers, which indicates branching arising through the formation of side chains. Huggins' constant for the mixture of PVC and BMR lay between the values of this constant for the individual polymers, and was almost additive.

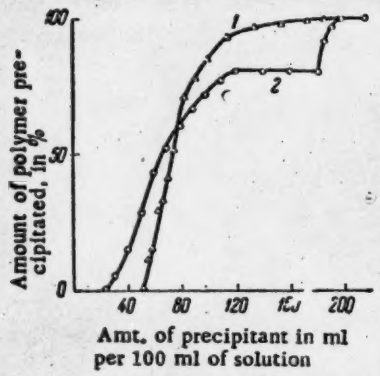


Fig. 1. Turbidimetric titration of solutions of polymers in a dimethylformamide – acetone mixture with methyl alcohol containing 5% water: 1) Graft copolymer of vinyl chloride (38.4%) on BMR-5 (61.6%); 2) mechanical mixture of PVC (33.2%) + BMR-5 (66.8%).

The coefficient f, which expressed the degree of interaction of the monomer with the polymer, shows that more than 60% of the monomer reacted with the polymer.

The turbidimetric titration was carried out by placing a solution of the polymer in dioxane or a mixture of dimethylformamide and acetone (C = 0.005%) in a T-shaped cell and back-titrating with a mixture of isopropyl alcohol and water (3 : 1) or methanol and water (19 : 1) while automatically feeding the precipitant at a constant rate of 3.33 ml/minute. The optical system of an FNK-51 nephelometer and EPP-09 recording potentiometer were used to measure the turbidity.

As seen from Fig. 1, separate precipitation occurred during the titration of the mixture of polymers, while the curve for the precipitation of the sample obtained by polymerization of vinyl chloride in BMR latex indicates the presence of graft copolymer.

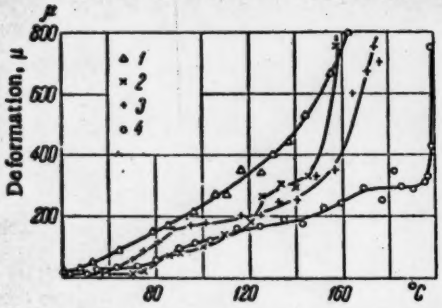


Fig. 2. Thermomechanical properties of the BMR-PVC graft copolymer as compared to those of a mixture of the polymers and of the individual polymers. 1) Copolymer of BMR (95 parts by wt.) and methacrylic acid (5 parts by wt.); 2) polyvinyl chloride (PVC); 3) mixture of BMK + PVC (1 : 1); 4) BMR – PVC graft copolymer (1 : 1).

Investigation of the effect of monomer-polymer ratio, of the polymerization modifier, and of the temperature on the yield and properties of the graft copolymers showed that an increase in the amount of vinyl chloride in the mixture of components leads to an increase in the coefficient f, which expresses the degree of incorporation of monomer, and in the yield of graft copolymer (see Table 2).

The addition of a modifier (CCl_4, CHI_3) sharply decreased the yield of graft copolymer, obviously by inactivation of part of the macroradicals.

An investigation of the thermomechanical properties with a V. A. Kargin apparatus showed that the graft copolymers, in contrast to the mixture of homopolymers of the same composition, went into the viscous-flow state at a significantly higher temperature (T_f = 190 instead of 135°), but there was little difference in T_g (see Fig. 2).

A change in the VC : BMR ratio in the graft copolymers from 1 : 1 to 4 : 1 sharply increased T_g (from 50 to 80°) and decreased T_f (from 190 to 155°).

Along with the investigation of the graft copolymers with a BMR main chain and PVC side chains, copolymers with the reverse order of grafting were synthesized.

For this purpose, a mixture of butyl methacrylate (95 parts by weight) and methacrylic acid (5 parts by weight) was added to a polyvinyl chloride latex at a PVC : BMR ratio of 1:12. After the monomers had been emulsified in the PVC latex for four hours at 60°, the initiator [0.5% $(NH_4)_2S_2O_8$] was introduced, and polymerization was carried to practically complete conversion of the monomers. The resulting product was purified and investigated in the same manner as the BMR – PVC graft copolymers.

In the case of BMR grafted to PVC, there was a 7- to 8-fold increase in the bound chlorine in the fraction going into solution during a 50-hour extraction with acetone or with an azeotropic mixture of the composition chloroform (47%) – acetone (30%) – methanol (23%).

TABLE 2

Initial VC-BMR ratio, wt.	Copolymer analysis							
	before extraction		after extraction					
	Cl, %	η_{sp}	copol, %	Cl, %	η_{sp}	f	T_g	T_f
1:1	23,4	0.70	71,0	26,2	1,16	0,650	50	190
2:1	34,5	0,57	74,1	35,3	0,92	0,705	75	170
4:1	39,8	0.63	82,0	41,2	0,67	0,753	80	155
1:1*	23,9	0,45	52,8	28,4	—	0,455	58	160
4:1*	44,8	0,31	46,7	48,7	0,37	0,315	63	140
PVC	56,0	0,25	—	—	—	—	70	140
BRM	—	0,40	—	—	—	—	40	—
PVC + BMR **	27,5	0,40	55,9	46,5	0,43	—	57	135

* Prepared in the presence of CCl_4 (10 wt. % of the monomer).

** Mechanical mixture of PVC + BMR-5 = 1:1.

Such an increase in solubility was apparently due to the formation of more readily solvating BMR side chains on the macromolecules of the low-molecular-weight fraction of PVC.

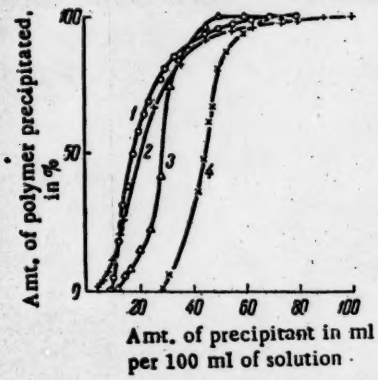


Fig. 3. Turbidimetric titration of solutions of polymers in dioxane with a mixture of isopropyl alcohol and water. 1) PVC – BMR graft copolymer; 2) PVC; 3) BMR–PVC graft copolymer; 4) BMR.

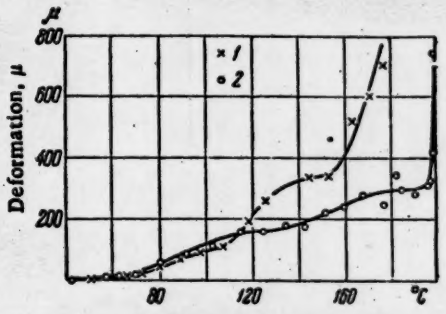


Fig. 4. Thermomechanical properties of graft copolymers of BMR and PVC with both the direct and reverse order of grafting. 1) Graft of BMR on PVC (1:1); 2) graft of PVC on BMR (1:1)

In Fig. 3 are presented the titration curves for solutions of "direct" (BMR–PVC) and reverse (PVC–BMR) graft copolymers.

The points for the initiation of precipitation for the "direct" and "reverse" graft copolymers are very close together and lie between the points of initial precipitation for the homopolymers.

Figure 4 indicates a sharp difference in the thermomechanical properties of the copolymers prepared by direct and reverse grafting at practically identical component ratios and values of f. Grafting of BMR on PVC gave products with a higher T_g and a lower T_f than for the polymer prepared by the reverse order of grafting. Thus, a comparison of the thermomechanical properties of the "direct" and "reverse" graft copolymers leads to the conclusion that under otherwise equivalent conditions, the nature of the main chain has the greatest effect on glass temperature, while the side chains responsible for the spatial structure have the predominant effect on the temperature interval of viscous flow.

An increase in the length of the side chains increases their effect on T_g of the copolymer (see Table 2), since in this case the flexibility of the main chain depends to a greater extent on the flexibility and intermolecular interaction of the side chains.

It should also be noted that the nature of the thermomechanical curves for the graft copolymers differs from the nature of the analogous curves for the mixture of homopolymers by the presence of two plateaus (see curves of Figs. 2 and 4).

The BMR – PVC graft copolymers are of great practical interest, since they combine the intrinsic high adhesion and light stability of BMR with the high abrasion resistance, resistance to water, gasoline and oil, chemical resistance, and incombustibility of polyvinyl chloride.

LITERATURE CITED

[1] A. A. Berlin, Russian Patent 70763, class 39B, 402, October 11, 1946; Russian Patent 73031, class 39, 4202, October 19, 1946; Russian Patent 68062, 39, 4202, April 15, 1946; Russian Patent 77731, 39, November 23, 1948.

[2] P. Compagnon and J. Le Bras, Rev. Gen. Cautch. 24, 4 (1947); French Patent No. 972,455 (1951).

[3] A. A. Berlin and G. A. Makarova, J. Gen. Chem. 21, 138 (1951). *

[4] A. A. Berlin, Coll. Progress in the Chemistry of Polymers,** (1957), p. 13.

[5] M. S. Akutin, Chem. Sci. and Ind. 2, 5, 585 (1957).

[6] P. P. Padchenko, Rubber and Resins, 16, 7, 13 (1957).

[7] J. Henstenberg, Zs. Electrochem. 60, 3, 236 (1956).

[8] H. W. Melville, Polym. Sci. 16, 505 (1955).

Received April 1, 1958

* Original Russian pagination. See C. B. Translation.

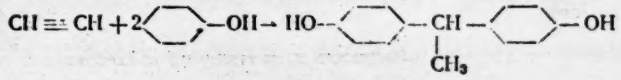
** In Russian.

ALKYLATION OF PHENOL WITH ACETYLENE AT ELEVATED PRESSURE

V. L. Vaiser and V. D. Riabov

(Presented by Academician A. V. Topchiev, March 22, 1958)

In previous work [1-5], we carried out for the first time a detailed study of the alkylation of phenol with acetylene at atmospheric pressure. Water and ethyl alcohol were used as the solvents for the phenol [2]; it was shown that the reaction proceeds more selectively with water as the solvent. It was found [3] that in aqueous medium, the reaction of acetylene with phenol proceeds through an intermediate stage in which acetaldehyde is formed. The yield of 1,1-(4,4'-dihydroxy)diphenylethane from this reaction does not exceed 50% of that calculated from the stoichiometry:



In order to determine the effect of pressure and to establish the optimum conditions for alkylation under pressure, experiments were carried out in a rotating autoclave.

Carrying out the reaction at an elevated pressure has the following advantages: the acetylene concentration in the gas phase is many times greater than at atmospheric pressure; the concentration of acetylene in the liquid phase is increased owing to the increased solubility of the acetylene; acetylene losses are negligible.

The essential disadvantage of carrying out the reaction in a rotating autoclave is that it is impossible to maintain the pressure at a specific level.

Conditions and methods for the use of acetylene under pressure were first studied by A. E. Favorsky and M. F. Shostakovskii [6] in connection with vinylation reactions and by A. D. Petrov and L. I. Antsus [7] in connection with the hydropolymerization of acetylene; there are a number of patents describing the synthesis of vinyl ethers of high-molecular-weight products under acetylene pressure, the acetylene being diluted with nitrogen for safety.

But, as was originally shown by the work of Soviet investigators, safety during the course of the reaction can be provided without having recourse to special dilution of the acetylene; dilution of the acetylene is provided during the course of the reaction by the vapors of the materials in the reaction mixture. The advantage of this method is the absence of a nitrogen charge and the resulting high reaction rate owing to the higher concentration of acetylene in the reaction zone.

The method was successfully used in our work. All experiments were carried out in a rotating, stainless steel autoclave having a volume of 250 cc. The temperature inside the autoclave was measured with an iron-constantan thermocouple and a millivoltmeter. The rate of rotation of the autoclave and the temperature were regulated by rheostats.

A mixture of phenol, solvent, and $H_3PO_4 \cdot BF_3$ and HgO as a catalyst, was charged in the autoclave. The autoclave was then purged with cylinder acetylene to remove the air. After the purging, it was charged with acetylene to a pressure of 20 atm. and rotation was started. Simultaneously, the electric heater was switched on. Since the acetylene was absorbed at a high rate, there was a considerable drop in pressure in the autoclave while the required temperature was being reached.

Therefore, in succeeding experiments the appropriate temperature was first attained, and then the acetylene was introduced.

At the conclusion of the reaction, the temperature was held at about 70° in order to reduce the viscosity of the reaction products and facilitate their discharge from the autoclave.

The reaction products were separated from the aqueous layer and cooled. The precipitated crystals were filtered on a vacuum filter, washed with cold water to remove the phenol, dried, and weighed. In all cases, the melting point of the crystals after recrystallization from water was 120-122°. A mixture of the crystals with pure 1,1-(4,4'-dihydroxy) diphenylethane showed no depression of the melting point.

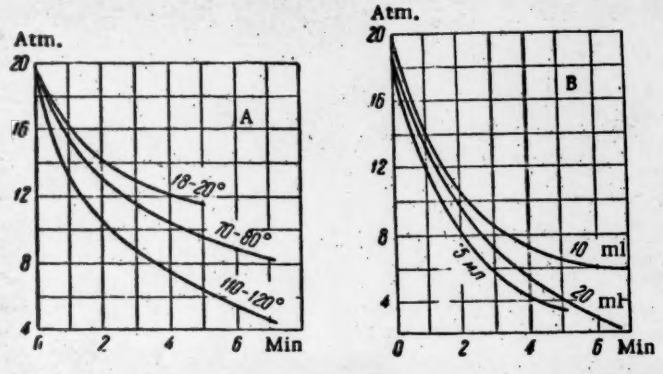


Fig. 1. Variation in acetylene absorption rate with temperature (A) and with the amount of catalyst (B).

The optimum conditions for the reaction were determined from the yield of crystals and the acetylene absorption rate.

Experiments to study the effect of temperature were carried out in aqueous solution in four temperature intervals: 18-20°, 70-80°, 90-100°, and 110-120°.

The reaction time (66 minutes) and the ratio of reaction components remained constant in all cases. A mixture of 50 g of phenol, 50 ml of distilled water, 2 g of HgO, and 20 ml of $H_3PO_4 \cdot BF_3$ was allowed to stand for a day, stirred vigorously, and was then used in the reaction.

The reaction rate was estimated from the acetylene absorption rate, which was determined from the change in pressure with time (atm./minute).

TABLE 1

Expt. No.	Temp. °C	Initial pressure, atm.	Pressure change, Δp (atm) in the time intervals					Final pressure, atm.	Acetylene absorbed, g *	Yield	
			1 min	2 min	2 min	2 min	4 min			g	% of theoretical
1	18—20	20	4	3	1,0	—	0,5	11,5	1,78	0	—
2	70—80	20	4,5	3,5	2,0	2,0	3,5	3,0	2,35	3	15,8
3	90—100	20	—	—	—	—	—	5,0	1,93	7	44,0
4	110—120	20	7,0	3,5	3,5	1,5	—	2,5	2,05	11	65,0

* The amount of acetylene absorbed was calculated by means of the modified Mendeleev-Clapeyron equation taking into account the compressibility factor.

The variation in acetylene absorption rate with temperature is shown in Fig. 1, a and Table 1. It is seen from Fig. 1, a that the maximum acetylene absorption rate occurred in the temperature interval 110-112° and

the minimum was at 18-20°. The maximum reaction rate occurred at a pressure of 20-16 atm. The higher the temperature, the lower was the pressure corresponding to the minimum absorption rate.

From the results of the experiments, it is seen that the optimum reaction conditions are a temperature of 110-120° and a pressure of 20-16 atm.

The effect of the amount of catalyst was studied at 110-120°. Treatment of the reaction products was as before. In Table 2 are presented the experimental results characterizing the dependence of the yield of 1,1-(4,4'-dihydroxy) diphenylethane on the amount of catalyst.

TABLE 2

Expt. No.	Catalyst*	Initial pressure, atm	Pressure change, Δp (atm) in the time intervals				Final pressure, atm.	Acetylene absorbed, g	Yield	
			1 min	2 min	2 min	2 min			g	% of theoretical
7	27,2	20	7,0	5,5	3,5	1,5	2,5	2,06	10,4	61,2
8	15,1	20	6,5	5,0	2,0	0,5	3,0	2,16	9,5	53,2
9	8,3	20	8,0	6,0	2,5	0,5	3,0	2,28	8,7	48,0

* The amount of mercuric oxide was held constant at 2 g.

It is seen from Table 2 that the yield decreases slightly with a decrease in the amount of catalyst. The yield decreased by 8.5% with a decrease in the amount of catalyst from 27.2 to 15.1%.

The dependence of the acetylene absorption rate on the amount of catalyst is shown in Fig. 1, b. The rate of acetylene absorption was approximately the same in all cases.

As shown by the experiments at a temperature of 110-120°, the catalyst solution acquires a bright green color and becomes transparent during the course of the reaction (the mercuric oxide dissolved completely; mercury precipitates were not observed).

TABLE 3

Expt. No.	Origin of catalyst solution	Initial pressure, atm.	Pressure change, Δp (atm) in the time intervals				Final pressure, atm.	Acetylene absorbed, g	Yield	
			1 min	2 min	2 min	2 min			g	% of theoretical
10	From Expt. No. 8	20	4,0	2,5	0,3	0,5	12	0,99	5	62
11	From Expt. No. 10	20	7,5	6,8	2,7	—	2,5	2,06	11	65
12	From Expt. No. 11	20	7,0	6,0	3,0	—	3,5	2,02	7	60

On long standing and heating of the solution, the color and transparency did not change. Several experiments were carried out at a temperature of 110-120° for the purpose of studying the catalytic activity of this solution. 50 g of phenol was added to 70 cc of a solution of used catalyst (from Experiment No. 8). The mixture was placed in the autoclave, where the reaction was carried out for a period of 1.1 hours. After appropriate treatment of the reaction products, 5 g of crystals were isolated. In a succeeding experiment, 70 cc of used catalyst solution was also used, but 2 g of mercuric oxide was added. 11 g of crystals was obtained in this experiment. Another 2 g of mercuric oxide was added to this catalyst solution, and 7 g of crystals was obtained. The results are presented in Table 3.

It is seen from Table 3 that the once-used catalyst has approximately half the activity of fresh catalyst (judging the activity of the catalyst from the amount of acetylene absorbed per unit time); however, the yield (in percent of theoretical) based on reacted acetylene remained high, which indicates that side reactions did not occur to any great extent.

The addition of mercuric oxide to the used catalyst solution reduced its activity. Subsequent use of the catalyst solution with added mercuric oxide leads to a gradual decrease in activity.

LITERATURE CITED

[1] V. L. Vaiser, Proc. Acad. Sci. USSR 70, 4 (1950).

[2] V. D. Riabov and V. L. Vaiser, Coll. 9th Scientific-Technical Conference of the Moscow Petroleum Institute,* (1954).

[3] V. L. Vaiser and V. D. Riabov, Proc. Acad. Sci. USSR 100, 2 (1956),**

[4] V. L. Vaiser, Proc. Acad. Sci. USSR 97, 4 (1954).

[5] V. L. Vaiser, Proc. Acad. Sci. USSR 103, 5 (1955).

[6] A. E. Favorskii and M. F. Shostakovskii, J. Gen. Chem. 13, 1 (1943).

[7] L. I. Antsus and A. D. Petrov, Bull. Acad. Sci. USSR, Div. Chem. Sci. (1942), p. 125.

I. M. Gubkin Moscow Petroleum Institute

Received March 20, 1958

* In Russian.

** Original Russian pagination. See C. B. Translation.

INFRARED ABSORPTION SPECTRA OF HYDROXYBENZYLAMINES

L. A. Igonin and S. I. Bass

(Presented by Academician V. A. Kargin, April 3, 1958)

According to work carried out by a number of investigators [1] using as models mono- and disubstituted phenols, hydroxybenzylamines are formed as intermediate reaction products during the curing of phenol-formaldehyde resins with hexamethylenetetramine. Hydroxybenzylamines are polynuclear compounds, the phenol nuclei of which are connected by dimethyleneamine ($-CH_2-NH-CH_2-$) and trimethyleneamine [$N(CH_2-)_3$] bridges. It is assumed that these bridges are converted under the effect of thermal excitation into methylene and azomethine bridges during the curing process.

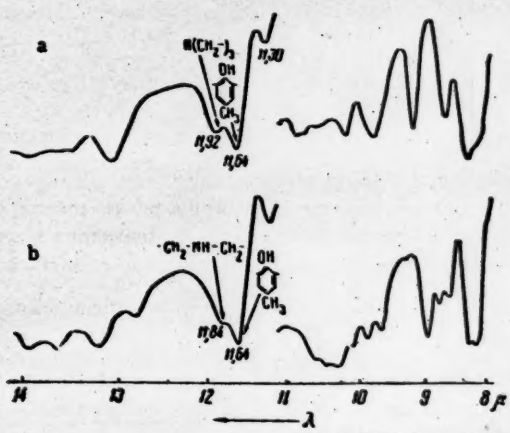
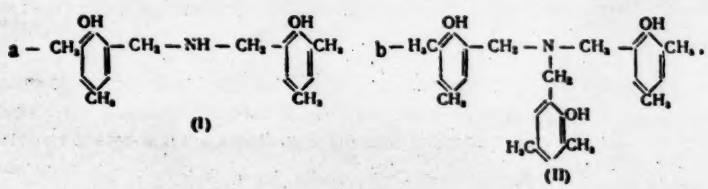


Fig. 1. Infrared absorption spectra of:



Confirmation of the above-indicated concepts by means of infrared spectroscopy is of considerable interest. In spite of the fact that infrared spectroscopy is one of the few methods which can be used for the structural investigation of the infusible and insoluble cure products, very little work devoted to this problem has been published. Work has been published on the study of the absorption spectra of a number of substituted phenols and certain Novolak and resol resins. However, no work has appeared which is related to the cure processes of phenol-formaldehyde resins under the influence of hexamethylenetetramine.

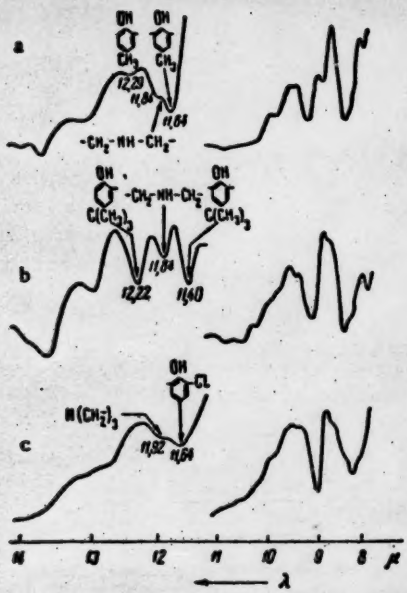
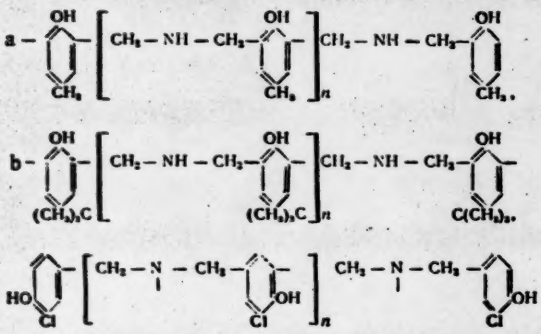
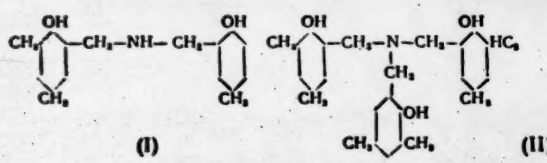


Fig. 2. Infrared absorption spectra of polynuclear hydroxybenzylamines:



The present communication reports the results of an investigation of the absorption spectra in the infrared region of certain hydroxybenzylamines prepared by the interaction of phenol and its mononuclear derivatives with hexamethyleneaminetetramine. In Fig. 1 are presented the absorption spectra of two model substances: 2,2'-dihydroxy-3,5,3',5'-tetramethyldibenzylamine (I) and the corresponding trihydroxybenzylamine (II):



(I) (II)

These products were prepared from 2,4-xylenol by the method described in [3].

On the basis of the available literature data [2], it is possible to identify some of the more intense bands in the absorption spectra of these compounds. Thus, the absorption band in the region of 11.6μ, which is present in the spectra of both compounds, must be identified with the tetrasubstituted benzene structure. The intense band in the region of 8.3μ is usually assigned to O—H deformation vibrations. Besides these bands, the

rather intense bands which we observed in the region of 11.8 and 11.92μ are of great interest. The first of these is present in the spectrum of dibenzylamine, while the second is found in the spectrum of tribenzylamine, both bands being located close to the intense band characteristic of the tetrasubstituted benzene structure.

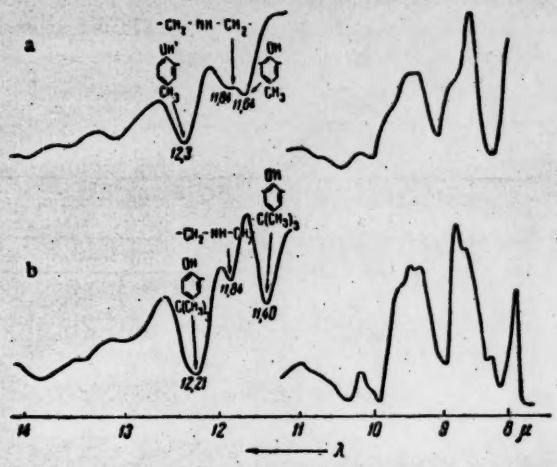
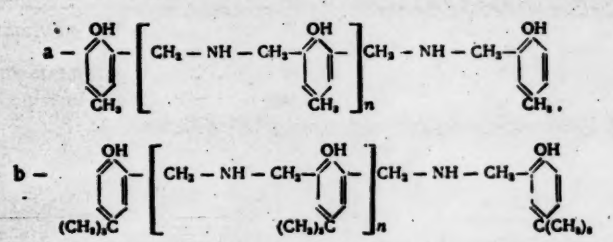


Fig. 3. Infrared absorption spectra of high-molecular-weight hydroxybenzylamines:



The absorption spectra of polynuclear hydroxybenzylamines are presented in Fig. 2. These hydroxybenzylamines were prepared by heating to 140-160° a carefully ground mixture of the appropriate phenol with hexamethylenetetramine; they are comparatively low-molecular-weight compounds [4]. Besides the absorption bands indicated above, which are associated with tetrasubstituted benzene and with the hydroxyl group, intense bands in the region of 12.2μ are present in the spectra of the polynuclear hydroxybenzylamines; these bands are associated with a trisubstituted benzene ring, the terminal groups of the hydroxybenzylamines. In the spectra of all of the hydroxybenzylamines prepared from phenol and its p-substituted derivatives there is present an absorption band in the region of 11.84μ, corresponding to a dimethyleneamine bridge, $-CH_2-NH-CH_2-$, while in the spectrum of the polymer prepared from o-chlorophenol there is an absorption band in the region of 11.92μ, corresponding to a trimethyleneamine bridge, $N(CH_2-)_3$. These results are in agreement with the data of a number of authors [1], according to which p-substituted phenols react with hexamethylene tetramine with the formation primarily of dibenzylamines, while o-substituted phenols form primarily tribenzylamines.

Figure 3 presents the absorption spectra of high-molecular-weight hydroxybenzylamines prepared by the interaction of phenols with hexamethylenetetramine in solution in biphenyl; these spectra are basically repetitions of the absorption spectra of polynuclear hydroxybenzylamines presented in Fig. 2. In the absorption spectra of the polyhydroxybenzylamines, the bands in the 12.2μ region, which are associated with the terminal groups, are considerably weakened; however, they have not completely disappeared, and this is apparently due to the considerable degree of branching of these polymers.

We see that the absorption bands characteristic of dimethyleneamine and trimethyleneamine bridges also appear in the absorption spectra of the polyhydroxybenzylamines; these spectra are presented in Fig. 3.

Thus, the absorption bands in the 11.84 μ and 11.92 μ regions of the spectra of the model hydroxybenzylamines, due to the presence of dimethyleneamine and trimethyleneamine bridges, are also present in the spectra of polynuclear hydroxybenzylamines and polyhydroxybenzylamines. There arises the possibility of using these characteristic absorption bands in structural investigations of curing processes of phenol-formaldehyde resins, in those cases where curing proceeds through a stage in which hydroxybenzylamines are formed.

LITERATURE CITED

[1] R. W. Martin, The Chemistry of Phenolic Resins (New York, 1956).

[2] R. E. Richards and H. W. Thompson, J. Chem. Soc. (1947), p. 1260; H. W. Thompson and P. Torkington, Trans. Farad. Soc. 41, 246 (1945).

[3] K. Hultzsch, Chem. Ber. 82, 16 (1949).

[4] A. Zinke, G. Zigeuner, G. Weiss, and W. Leupold-Löwenthal, Monatsh. Chem. 81, 1098 (1950).

Plastics Scientific Research Institute

Received February 11, 1958

ON THE ACTION OF AMINES AND AMMONIA ON ISOAMYLBORON DICHLORIDE

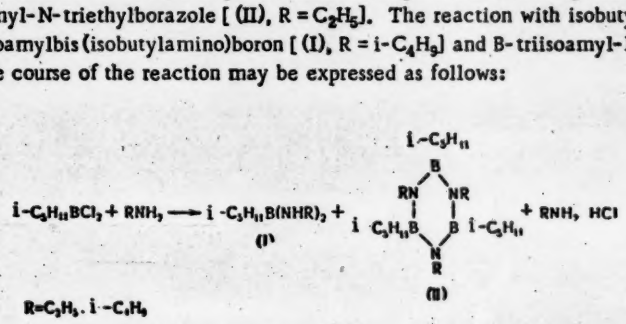
B. M. Mikhailov and T. K. Kozminskaia

(Presented by Academician B. A. Arbuzov, April 4, 1958)

A study of the reaction between phenylboron dichloride and amines has shown that the course of the reaction is determined by the nature of the amine. The action of ethylamine on phenylboron dichloride gives phenylbis (ethylamino) boron and B-triphenyl-N-triethylborazole; with aniline, phenylboron dichloride gives only phenylbis (phenylamino) boron [1], while the action of ammonia smoothly converts the dichloride to B-triphenylborazole [2].

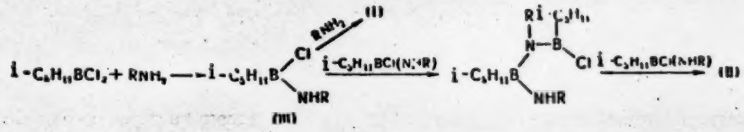
It appeared to be of interest to study the behavior of alkylboron dichlorides with respect to the action of amines and ammonia. The specific compound selected for study in the investigation was isoamylboron dichloride, which was prepared by a previously described method comprising the action of phosphorus pentachloride on esters of alkylboric acids [alkaneboronic acids] [3].

Isoamylboron dichloride was converted by the action of ethylamine to isoamylbis (ethylamino)boron [(I), $R = C_2H_5$] and B-triisoamyl-N-triethylborazole [(II), $R = C_2H_5$]. The reaction with isobutylamine proceeded analogously yielding isoamylbis (isobutylamino)boron [(I), $R = i\text{-}C_4H_9$] and B-triisoamyl-N-isobutylborazole [(II), $R = i\text{-}C_4H_9$]. The course of the reaction may be expressed as follows:



$R = C_2H_5, i\text{-}C_4H_9$

In the first stage of the process, there is evidently formed the alkyl (alkylamino) boron chloride (III), which then both reacts with another molecule of the amine with the formation of (I), and also condenses to the borazole (II):



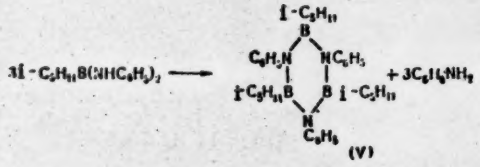
Substituted alkylbis (diamino)borons were previously obtained by one of us and T. A. Shchegoleva by the action of amines on esters of alkylchloroboric acids [alkaneboronic acid chlorides] [4]. The borazoles obtained in this work are the first representatives of unsymmetrical hexaalkylborazoles.

The action of aniline on isoamylboron dichloride gave isoamylbis (phenylamino)boron (IV).

$$i\text{-}C_5H_{11}BCl_2 + 4C_6H_5NH_2 = i\text{-}C_5H_{11}B(NHC_6H_5)_2 + 2C_6H_5NH_2 \cdot HCl$$

(IV)

At 300-360°, the latter was converted in good yield to B-triisoamyl-N-phenylborazole (V), which is a representative of the previously unknown B-trialkyl-N-triarylborazoles.

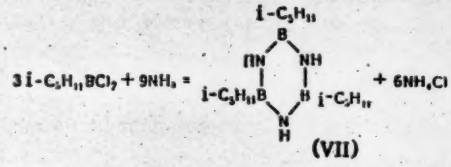


(V)

The reaction between isoamylboron dichloride and diethylamine proceeded with the formation of isoamylbis(diethylamino)boron (VI).

$$i\text{-}C_5H_{11}BCl_2 + 4NH(C_2H_5)_2 = i\text{-}C_5H_{11}B[N(C_2H_5)_2]_2 + 2(C_2H_5)_2NH \cdot HCl$$

In passing ammonia through an ether solution of isoamylboron dichloride, B-triisoamyl borazole (VII) is formed.



(VII)

B-trialkyl compounds of borazole have been previously prepared by heating alkyldiboranes and trialkylborons with ammonia at 200-330° [5]. Booth and Kraus [6] reported that they obtained butylboronimine, probably in the form of a polymer, by the action of sodium in liquid ammonia on n-butylboron dichloride.

EXPERIMENTAL

All operations were carried out in a nitrogen atmosphere.

1. Esters of Isoamylboric Acid

Esters of isoamylboric acid [3-methyl-1-butaneboronic acid] have been prepared by Snyder et al. [7] by the action of isoamylmagnesium chloride on trimethyl borate, with subsequent esterification of the isoamylboric acid with the appropriate alcohols.

The isobutyl ester of isoamylboric acid was obtained in a yield of 50% of theoretical. B. p. 105-106°/12.2 mm, d^{20}_4 0.8167; n^{20}_D 1.4156.

Found %: C 68.43, 68.54; H 12.69, 12.55; B 4.67, 4.74. $C_{13}H_9BO_2$. Calculated %: C 68.42; H 12.79; B 4.74.

The cyclohexyl ester of isoamylboric acid was obtained in a yield of 40% of theoretical. B. p. 146.5 to 147° (5.5 mm), d^{20}_4 0.9137; n^{20}_D 1.4600.

Found %: C 73.01, 72.94; H 11.99, 11.86; B 3.64, 3.44. $C_{13}H_{33}BO_2$. Calculated %: C 72.91; H 11.79; B 3.86.

2. Isoamylboron Dichloride

187.5 g (0.9 mole) of phosphorus pentachloride was added gradually over a period of 3 hours and with stirring to 102.7 g (0.45 mole) of the isobutyl ester of isoamylboric acid. The first half of the chloride reacted

exothermically, but the reaction mixture was heated during the addition of the second half. At the conclusion of the PCl_5 addition, the reaction mixture was refluxed 1.5 hours, and was then fractionally distilled in a column.

43 g (61%) of isoamylboron dichloride was obtained, b. p. 124-125.5°, d^{20}_4 0.9940.

Found %: C 39.45, 39.48; H 7.34, 7.26; B 7.10, 6.92; Cl 45.95. $C_5H_{11}BCl_2$. Calculated %: C 39.28; H 7.26; B 7.07; Cl 46.39.

The material was air-hypergolic.

60.9 g of isobutyl chloride and 123.4 g of $POCl_3$ were obtained in the experiment.

3. Isoamylbis(ethylamino)boron

B-triisoamyl-N-triethylborazole. 50 ml of ether was added slowly and with stirring to 20.1 g (0.13 mole) of isoamylboron dichloride which had been cooled to − 40°. The resulting ether solution was added over a period of 45 minutes to a stirred mixture of 35.2 g (0.77 mole) of ethylamine and 300 ml of ether, which had been cooled to − 50°. The reaction mixture was allowed to stand overnight. The precipitated ethylamine hydrochloride was filtered, the solvent was distilled, and the residue was fractionated. There were obtained:

1) 7.1 g (31.6%) of isoamylbis(ethylamino)boron with a b. p. of 94-94.5°/19 mm, d^{20}_4 0.8040; n^{20}_D 1.4337.

Found %: C 63.53, 63.76; H 13.57, 13.56; B 6.40, 6.73. $C_9H_{23}N_2$. Calculated %: C 63.55; H 13.62; B 6.36.

2) 7.5 g (47.7%) of B-triisoamyl-N-triethylborazole, which crystallized on standing. B. p. 113 to 114°/0.06 mm, m. p. 43-45°.

Found %: C 67.00, 67.03; H 12.83, 12.70; B 8.55, 8.54. $C_{21}H_{48}B_3N_3$. Calculated %: C 67.24; H 12.90; B 8.66.

Molecular weight: found 384, calculated 375.

The substance was readily soluble in ether, benzene, and isopentane; it was stable in air.

4. Isoamylbis(isobutylamino)boron

B-triisoamyl-N-triisobutylborazole. 19.7 g (0.13 mole) of isoamylboron dichloride and 44 g (0.61 mole) of isobutylamine were used in an experiment which was carried out as described above. The following compounds were obtained:

1) 11.1 g (38.1%) of isoamylbis(isobutylamino)boron with a b. p. of 112-113° (7 mm); d^{20}_4 0.8028; n^{20}_D 1.4381.

Found %: C 69.30, 69.14; H 13.67, 13.74; B 4.74, 4.78. $C_{13}H_{31}BN_2$. Calculated %: C 69.02; H 13.81; B 4.78.

2) 9.6 g (50.4%) of B-triisoamyl-N-triisobutylborazole with a b. p. of 126-128°/0.06 mm, m. p. 53-55°.

Found %: C 70.21, 70.20; H 12.95, 12.94; B 7.36, 7.38. $C_{27}H_{60}B_3N_3$. Calculated %: C 70.61; H 13.17; B 7.07.

Molecular weight: found 458, calculated 459.

26.5 g of isobutylamine hydrochloride was obtained in the experiment.

5. Isoamylbis(diethylamino)boron

The experiment was carried out similarly to those described above. 14 g (0.09 mole) of isoamylboron dichloride and 30 g (0.41 mole) of diethylamine were used. There were obtained 17.1 g of diethylamine hydrochloride and 10.4 g (50%) of isoamylbis(diethylamino)boron with a b. p. of 103-104°/9 mm; d^{20}_4 0.8192; n^{20}_D 1.4488.

Found %: C 68.59, 68.32; H 13.48, 13.51; B 5.14, 5.14. $C_{13}H_{31}BN_2$. Calculated %: C 69.02; H 13.81; B 4.78.

6. Isoamylbis(phenylamino)boron

A mixture of 19.1 g (0.125 mole) of isoamylboron dichloride and 50 ml of ether was added at 0° to a solution of 46.9 g (0.504 mole) of aniline in 300 ml of ether; the addition was carried out over the course of an hour while stirring. The reaction mixture was then stirred at room temperature for 2 hours. The aniline hydrochloride precipitate (31 g) was washed twice with ether and repeatedly extracted with hot benzene. The solvent was distilled from the filtrate, and the residue was heated for an hour at 90°; the small amount of aniline hydrochloride which precipitated was filtered, and the filtrate was fractionated. 18.8 g (46.6%) of isoamylbis(phenylamino)boron was obtained, b. p. 142-143°/0.07 mm; d^{20}_4 0.9954; n^{20}_D 1.5700.

Found %: C 76.88, 76.61; H 8.68, 8.59; B 4.07, 3.98. $C_{17}H_{23}BN_2$. Calculated %: C 76.70; H 8.71; B 4.07.

7. B-triisoamyl-N-triphenylborazole

Isoamylbis(phenylamino)boron (11.1 g) was placed in a flask fitted with a downward-sloping condenser, and was heated on a metal bath. Distillation of aniline commenced at 300°; the temperature of the bath was gradually (over a period of 2 hours) increased to 365°. 3 g of aniline distilled. The residue, which crystallized at room temperature, was distilled under vacuum. 6 g (83.3%) of a yellowish, rapidly-solidifying substance with a b. p. of 178-185°/0.03 mm was obtained. After a second distillation, the B-triisoamyl-N-triphenylborazole boiled at 180-181°/0.03 mm and melted at 93.5-95.5°.

Found %: C 76.45; H 9.45; B 6.34. $C_{33}H_{48}B_3N_3$. Calculated %: C 76.33; H 9.32; B 6.25.

Molecular weight: found 475, calculated 519.

The substance was readily soluble in ether, benzene, and isopentane.

8. B-triisoamylborazole

A stream of dry ammonia was passed through an ether solution of isoamylboron dichloride (6.8 g in 150 ml ether) cooled to − 50°. After the reaction mixture had been stirred for an hour at room temperature, the precipitated ammonium chloride (4.4 g) was filtered and washed with ether. The ether was distilled from the filtrate, and the residue was distilled. 2.1 g (48.7%) of B-triisoamylborazole was obtained in the form of a colorless liquid with a b. p. of 114-115.5°/0.1 mm; d^{20}_4 0.8485; n^{20}_D 1.4538.

Found %: C 62.07, 61.80; H 12.43, 12.61; B 10.84. $C_{15}H_{36}B_3N_3$. Calculated %: C 61.93; H 12.47; B 11.16.

Molecular weight: found 282, calculated 291.

LITERATURE CITED

[1] B. M. Mikhailov and P. M. Aronovich, Bull. Acad. Sci. USSR, Div. Chem. Sci. (1957), 1123.*

[2] B. M. Mikhailov and T. V. Kostroma, Bull. Acad. Sci. USSR, Div. Chem. Sci. (1957), 1125.*

[3] B. M. Mikhailov and T. A. Shchegoleva, Bull. Acad. Sci. USSR, Div. Chem. Sci. (1957), 1080.*

[4] B. M. Mikhailov and T. A. Shchegoleva, Bull. Acad. Sci. USSR, Div. Chem. Sci. (1958), 777.*

[5] E. Wiberg, Naturwiss. 35, 182 (1948).

[6] R. Booth and C. Kraus, J. Am. Chem. Soc. 74, 1415 (1952).

[7] H. Snyder, J. Kuck, and J. Johnson, J. Am. Chem. Soc. 60, 105 (1938).

N. D. Zelinskii Institute of Organic Chemistry
Academy of Sciences, USSR

Received March 25, 1958

* Original Russian pagination. See C. B. Translation.

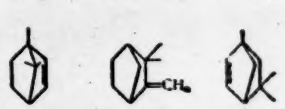
THE STEREOCHEMISTRY OF σ,π-CONJUGATION. AUTOOXIDATION IN RIGID ALLYL SYSTEMS

Academician A. N. Nesmeianov, K. A. Pecherskaia, A. N. Akhramovich, and L. M. Minakova

In our preceding papers on the spatial conditions for σ,π-conjugation [1], it was shown that in rigid bicyclic structures, C−H and C−Hg bonds at a bridge head and at the same time in an α-position relative to a carbonyl group are not activated by the carbonyl. The mercury in α-chloromercuricamphenilone or in mercuri-bis-α-camphenilone is not replaced by hydrogen through the action of acids, nor does it exchange with the radioactive mercury in Hg^{203} and $Hg^{203}Cl_2$, though such exchange occurs in α-mercurized ketones in which the mercury is not located at a bridge head. The α-hydrogen atom of camphenilone is not nitrosated, sulfonated, nor brominated. σ,π-Conjugation is usually disrupted in A−C−C=O systems in which the axis of the σ-bond and the π-plane are perpendicular. Activation of the C−H bond is observed in allyl systems, H−C−C=C. Along with heterolytic substitution (metalation), homolytic replacement of hydrogen (homolytic σ,π-conjugation [12]) is particularly peculiar to such systems (in contrast to H−C−C=O-systems). Thus, allylic hydrogen is replaced by the bromine of bromosuccinimide and is oxidized to peroxide by atmospheric oxygen − a reaction which proceeds by a chain mechanism. Examples of this are the oxidation of tetralin to the hydroperoxide [2] and the oxidation of cyclohexene [3], isopropylbenzene [4], Δ^3-p-menthene [5] and other terpenes, cyclenes, and alkylbenzenes.

The aim of the present work was to clarify whether the same conditions hold for the disruption of H−C−C=C conjugation as we have shown to hold for H−C−C=O conjugation.

We investigated the tendency toward oxidation by oxygen of terpene hydrocarbons in which (owing to the presence of a methylene bridge) the C−H bond in the α-position with respect to the double bond is sterically fixed with respect to the latter, namely: bornylene (I), camphene (II), and δ-fenchene (III).



(I) (II) (III)

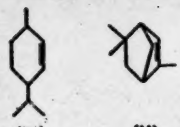
In the sense indicated, these hydrocarbons are compounds with a rigid structure. Two samples of bornylene and of camphene prepared by different routes were exposed to oxidation in order to exclude the possibility of error owing to impurities.

It was found that these three hydrocarbons did not absorb oxygen when they were subjected to oxidation by oxygen over a period of hours at 40, 60, and 80° and in the presence of such active initiators as cobalt and manganese stearates. After the attempted oxidations, the hydrocarbons were recovered from the solutions unchanged.

Under these conditions, nonrigid allyl systems are readily oxidized by molecular oxygen in the presence, or even in the absence of initiators.

For comparison, we carried out the autooxidation, under analogous conditions, of hydrocarbons with almost, but not quite, rigid* structures, namely, Δ^2-p-menthene (IV) and γ-fenchene (V).

* In the sense that the corresponding σ- and π-bonds are relatively fixed in space.



(IV) (V)

Δ^2-p-Menthene displayed the tendency toward oxidation by oxygen common to allyl groups. Thus, even at 40°, oxidation of Δ^2-p-menthene in the presence of cobalt stearate proceeded at a rate usual for similar hydrocarbons. After distillation of the unchanged Δ^2-p-menthene, the hydroperoxide resulting from the oxidation was distilled under vacuum, and was identified by its constants. In the case of γ-fenchene, oxidation at the methyl group is possible, and a lower rate is characteristic of such oxidation; however, this hydrocarbon was also capable of oxidation under rather mild conditions. It oxidized slowly at 60°, while oxidation of γ-fenchene proceeded at a normal rate at 80°.

Thus, the experiments described here show that homolytic σ,π-conjugation is influenced by the same steric factors as is heterolytic.

Indeed, the steric relationships of the CH-bonds and the double bonds studied in bornylene, fenchene, and camphene are the same as in camphenilone. In these hydrocarbons, owing to the presence of the methylene bridge, the axis of the σ-bond of the allylic hydrogen is rigidly fixed in a position nearly perpendicular to the axis of the π-bond.

It would be expected that in other hydrocarbons with an allylic system, the hydrogen atom in a rigid CH-link with its C—H bond fixed perpendicularly to the axis of the π-bond (as, for example, the α-hydrogen at the base of the bridge in the α-pinene molecule) would not be exchangeable. Therefore, the presently accepted scheme for the conversion of α-pinene to sobrerol [6] is subject to doubt and requires confirmation.

EXPERIMENTAL

The preparation of bornylene was carried out by two methods: 1) from borneol xanthate by the method of Chugaev [7], m. p. 101-102°; 2) from bornyl chloride by the method of Meerwein [8] with additional purification from admixed camphene, m. p. 104-105°. Literature data: m. p. 103-104° [7] and 103-104°, 107° [8].

The preparation of camphene was carried out: 1) by dehydration of isoborneol [9], m. p. 46-48°, b. p. 158-160°; 2) by dehydration of borneol [10], m. p. 47-49°. Literature data: m. p. 47-53° [10], m. p. 45-46°, b. p. 158-159° [11].

δ- and γ-Fenchenes were obtained by dehydration of fenchyl alcohol followed by multistage fractionation of the dehydration product [12]. δ-Fenchene: b. p. 139-141°, n^{20}_D 1.4510, d^{20}_4 0.8465. Literature data: b. p. 140-141°, n^{20}_D 1.4502, d^{20}_4 0.8397 [12]; b. p. 139-140°, n^{20}_D 1.4486, d^{20}_4 0.8433 [13]; b. p. 138.5-141°, n^{20}_D 1.4505, d^{20}_4 0.8376 [14].

γ-Fenchene: b. p. 146-147°, n^{20}_D 1.4589, d^{20}_4 0.8553. Literature data: b. p. 145-147°, n^{17}_D 1.46072, d^{20}_4 0.8547 [12].

Preparation of the Δ^2-p-menthene was carried out by reduction of α-terpinene [15]; b. p. 52-53.5°/10 mm, 154.5-157.5°/746 mm, n^{20}_D 1.4650. Literature data [15]: b. p. 55-56°/12 mm, n^{20}_D 1.4610.

In order to purify the hydrocarbons from traces of impurities which would affect the oxidation rate, all of the hydrocarbons investigated were repeatedly distilled over metallic sodium before oxidation.

The oxidation was carried out in an apparatus which consisted of a thermostatted bath in which the reaction vessel, a "bomb," was fastened; the bath was fitted with a mechanical stirrer. The bath was also fitted with a heater, which was connected into the circuit with the control contact thermometers through a relay. Oxygen was fed from a gas holder into a eudiometer tube through a Drechsel bottle containing a 50% solution of potassium hydroxide. From the eudiometer, the oxygen passed to the reaction vessel through a system of two columns and a Tishchenko bottle. One of the columns was filled with soda lime and calcium chloride, and the other only with calcium chloride. The Tishchenko bottle was filled with phosphorus pentoxide. All parts of the system were connected with rubber tubing. Before beginning an experiment, the system was tested for leaks. The

oxidations were carried out with oxygen at atmospheric pressure. A weighed amount of hydrocarbon dissolved in a solvent, and a weighed amount of an initiator (manganese or cobalt stearate), which comprised 0.2 wt. % of the substance being oxidized, were placed in the "bomb." A current of oxygen was passed through the system for 15 minutes to displace the air, and the "bomb" was then closed and placed in the thermostatted bath. When the reaction vessel had reached bath temperature, the oxygen level in the eudiometer was noted, and the amount of oxygen absorbed was then noted through equal time intervals; in Table 1, these values are corrected to normal conditions.

TABLE 1[1]

Hydrocarbon	Weight, g	Solvent	Oxidation, time, hrs.	Temp., °C	Vol. O_2 abs., ml	Notes
Bornylene from borneol	1.0	Benzene, 20 ml	6	40	1.8	a
	12.0	Benzene, 18 ml	6	60	1.06	b, c
	1.0	Naphthalene, 10 g	6	82	3.9	b
Bornylene from bornyl chloride	3.5	Benzene, 5 ml	6	60	3.7	b, c
Camphene from isoborneol	10.0	Benzene, 20 ml	6	40	2.5	a
	10.0	Same	6	50	2.3	a, d
	10.0	"	6	60	2.7	a, d
	10.0	Without solvent	9	60	4.0	a, d
	10.0	"	6	80	4.3	a, d
Camphene from borneol	1.0	Benzene, 2 ml	6	40	2.0	a, d
δ-Fenchene	1.0	Without solvent	8	60	2.7	a
	1.0	" "	6	80	3.5	a
Δ^2-p-Menthene	15.8	" "	18.5	40	907	a, b, d
γ-Fenchene	2.5	" "	13	60	35.0	a, c, f
	2.5	" "	21	80	165.4	a, c, f

Notes. 1. In blank experiments with 20 ml of benzene and 0.002 g of cobalt (or manganese) stearate at 60° for 6 hours, the decrease in the volume of oxygen was 3.7 ml.

2. a) with the addition of 0.2 wt. % manganese stearate.

b) with the addition of 0.2% cobalt stearate.

c) the bornylene recovered from the experiment had an m. p. of 93-95°.

d) the camphene recovered from the experiment had an m. p. of 47-48°.

e) 9.4 g of unoxidized menthene was recovered from the oxidized solution by vacuum distillation. The following fractions were collected on further distillation under vacuum: Fraction I: b. p. 50-52°/0.31 mm, n^{20}_D 1.4805; Fraction II: b. p. 72°/0.31 mm. A viscous, nondistillable residue remained in the flask. Fraction II was the hydroperoxide of Δ^2-p-menthene with the following constants: b. p. 72°/0.31 mm, d^{20}_4 1.0072, n^{20}_D 1.4960, MR_D 49.30. Calculated for $C_{10}H_{18}O_2$: MR_D 49.45; molecular weight: found 165, calculated 170.

f) the oxidation product was vacuum distilled. After distillation of the unoxidized γ-fenchene, 0.4 g of a fraction with a b. p. of 50°/0.1 mm and n^{20}_D 1.4765 was collected. The product liberated iodine from an acidified solution of potassium iodide.

LITERATURE CITED

[1] a) A. N. Nesmeianov, Scientific Reports Moscow State University 132, 5 (1950); b) A. N. Nesmeianov, D. N. Kursanov, K. A. Pecherskaia, and E. N. Parnes, Bull. Acad. Sci. USSR, Div. Chem. Sci. (1949), 592; c) A. N. Nesmeianov, K. A. Pecherskaia, and T. A. Tolstaia, Scientific Reports Moscow State University 132, 66 (1950); d) A. N. Nesmeianov and I. I. Kritskaia, Proc. Acad. Sci. USSR 121, 3 (1958).*

[2] R. Griegee and H. Logel, Chem. Ber. 84, 215 (1951).

[3] A. Farkas and E. Passaglia, J. Am. Chem. Soc. 72, 3333 (1950).

* Original Russian pagination. See C. B. Translation.

[4] H. Hock and S. Lang, Ber. 77, 257 (1944).

[5] H. Hock, Ber. 75, 300, 313 (1942); K. A. Pecherskaia and K. A. Krasnik, Scientific Reports Belorussian State University 20, 173 (1954).

[6] V. M. Nikitin, The Chemistry of Terpenes and Resin Acids,* (1952), p. 177.

[7] L. A. Chugaev, J. Russ. Phys. Chem. Soc. 36, 1039 (1904).

[8] H. Meerwein, Ber. 55, 2533 (1922).

[9] S. Moycho and F. Zienkowski, Lieb. Ann. 340, 61 (1905).

[10] M. Konovalov, J. Russ. Phys. Chem. Soc. 32, 361 (1900).

[11] E. Vagner, J. Russ. Phys. Chem. Soc. 28, 65 (1896).

[12] G. Komppa and R. Roschier, Lieb. Ann. 470, 129 (1929).

[13] S. S. Nametkin and A. K. Ruzhentseva, J. Russ. Phys. Chem. Soc. 48, 450 (1916).

[14] W. Qvist, Lieb. Ann. 417, 278 (1918).

[15] F. Semmler, Ber. 42, 526 (1909).

Institute of Heteroorganic Compounds
Academy of Sciences, USSR
V. I. Lenin Belorussian State University

Received April 21, 1958

* In Russian.

SOME DATA ON THE KINETICS OF THE THERMAL DECOMPOSITION OF ACETATES OF THE ALKALINE EARTH METALS

A. M. Rubinshtein and V. I. Iakerson

(Presented by Academician B. A. Kazanskii, April 14, 1958)

A study of the kinetics of the thermal decomposition of salts of carboxylic acids is of interest, because a knowledge of the kinetics can aid in establishing the role of the formation and decomposition of these compounds during vapor-phase ketonization of acids, a process which is used for the preparation of ketones, particularly unsymmetrical ketones. The kinetics of the decomposition of acetates is an example of such kinetics. According to Squibb [1] and Ipatieff [2], the vapor-phase ketonization of acetic acid can proceed through the intermediate formation of acetates with their subsequent decomposition into the metal carbonate and acetone. The same conclusion follows from the work of Nefedov and co-workers [3]; however, other concepts of the course of this reaction have been proposed [4-7].

An investigation of the kinetics of the decomposition of Mg, Ca, Sr, and Ba acetates appeared desirable in connection with the observation of a rare case of the formation of a bulk phase of an intermediate compound – the formation of acetate during the catalytic ketonization of CH_3COOH over Ca and Ba carbonates in a certain temperature interval; this observation was reported in [8], and was based on x-ray data. In the present work, we proposed to determine the initial decomposition temperatures and also the reaction rate constants and activation energies in order to compare them with the corresponding values for catalytic ketonization.

The rate of a chemical reaction cannot be predicted on the basis of the free energy change; however, for reactions having a single course, and, therefore, the same activated complex, there exists a definite connection between the kinetic and the thermodynamic characteristics of the reactions [9]. Free energy changes were calculated by the method of Temkin and Shvartsman [10] for the decomposition of acetates, $Me(CH_3COO)_2 = MeCO_3 + CH_3COCH_3$, for different cations and process conditions,

$$\Delta F_T^0 = \Delta H_{298} - T\Delta S_{298}^0 - T(M_0\Delta a + M_1\Delta b + M_2\Delta c + M_{-2}\Delta c'),$$

the values of ΔH^0_{298} and S^0_{298} being taken from the reference work of Rossini on thermodynamic properties and also from other sources; the missing values of the absolute entropies of Mg, Ca, Sr, and Ba acetates were calculated by approximate methods utilizing the formulas of Eastmen [11] and Wenner [12]. The course of the free energy changes with temperature, presented in Fig. 1, shows that the corresponding equilibrium yields vary in the following order $BaAc_2 > SrAc_2 > CaAc_2$ at 350-480° and $CaAc_2 > SrAc_2 > BaAc_2$ at 480-550°. Below 350°, ΔF becomes positive, the equilibrium constant becomes very small, and, in the case of the Ca, Sr, and Ba acetates, this represents a lower temperature limit for their decomposition. Similar calculations for Mg acetate show that the reaction does not go according to the above scheme. Indeed, in this case the decomposition proceeds with the formation of the oxide, as is shown by x-ray analysis.

We studied the decomposition of the acetates by a weight loss – temperature method using a vertical tube furnace with a CC thermocouple in the reaction zone; a small quartz or pyrex cup containing the material was suspended directly from torsion scales. The sample weight was about 1 mmole, and the temperature was raised 1 degree/minute up to the temperature at which reaction began. The weight loss – temperature curves of Fig. 2 show that the decomposition of $MgAc_2$ began at 300°, that of $CaAc_2$ at about 370°, and that of $SrAc_2$

at about 400°; these values are somewhat lower than the temperatures determined by Krönig [13]. Repetition of the experiments with preliminary dehydration of the acetates gave the same results.

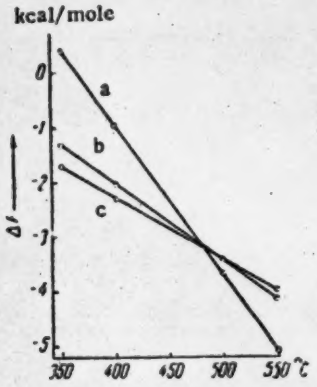


Fig. 1. The course of the free energy change with temperature for the decomposition of Ca (a), Sr (b), and Ba (c) acetates.

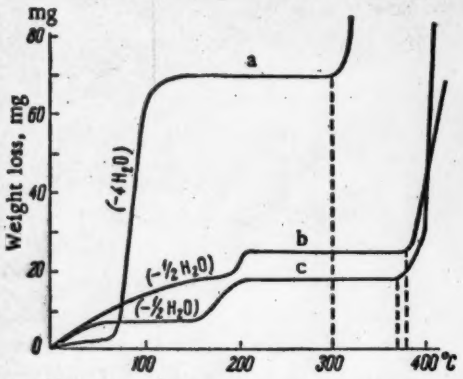


Fig. 2. Weight loss – temperature curves for the decomposition of Mg (a), Sr (b), and Ca (c) acetates.

While carrying out the experiments, the following complications in the course of the process, to which none of the investigators paid any attention, were observed: 1) the temperature regime of the process was not a steady state regime, and 2) some chemical changes occur in the presence of atmospheric oxygen. Indeed, after reaching the initial decomposition temperature the sample evolved heat, and its temperature, in the case of $CaAc_2$, for example, increased by 70°, after which it again fell to the temperature of the furnace. In special experiments in which the thermocouple was placed in the sample, it was found that with an over-all decomposition time of 10 minutes, this maximum increase in temperature occurred through 5 minutes. Further, visual observations after the reaction showed that the originally white material had darkened. If the reaction was interrupted by taking the sample from the furnace, the sample retained its dark color. We established by x-ray methods that at this stage of the reaction, the mass consisted of $CaAc_2$ with an admixture of a small amount of $CaCO_3$.

When the reaction was carried to completion, the carbonaceous deposit, which resulted from a side reaction, disappeared, apparently as a result of oxidation. The same picture was observed in experiments carried out in a stream of N_2 or CO_2 with an O_2 content of the order of 1%, but it was absent in experiments carried out in sealed tubes preliminarily purged with O_2-free nitrogen.

Kinetic curves for the decomposition of $CaAc_2$, plotted from the data obtained by us in the temperature interval 385-435°, are presented in Fig. 3, a. They show that the decomposition of this compound does not fall within the framework of the classical concepts of a monomolecular reaction. Only in the central portion of the curve is the first order equation obeyed. The decomposition rate was strongly dependent on the material forming the walls of the reaction vessel: it was greater in the Pyrex cup than in the quartz cup. The reaction rate decreased with a decrease in the amount of $CaAc_2$ from 1.7 to 0.6 mmole. In the Pyrex cup, the initially rapid reaction slowed down and then again accelerated. Upon the addition of Al_2O_3, the removal of heat was improved (the reaction is strongly exothermic), and the curves were more nearly linear. The activation energy, calculated from the linear central portion of the curves of Fig. 3, a, was 90 kcal/mole. Considering these anomalies, we are led to the conclusion that the kinetic curves presented by Read [14] (like the curves of Fig. 3, a) are pseudokinetic, and cannot serve as evidence in support of a radical mechanism for the decomposition of acetates, as proposed by Read.

Calculations according to the topokinetic equation of Erofeev [15], $\alpha = 1 - e^{-kt^n}$, in its logarithmic form (see Fig. 3, b) are considerably more rigorous. They describe the decomposition up to 100% for experiments carried out in the Pyrex cup, from 30-40 to 80-90% for experiments carried out in the quartz cup, and from 50 to 100% for experiments carried out with the addition of Al_2O_3; the acceleration of the reaction in the initial stage is probably due to spontaneous physical disintegration of the material.

The exponent n is close to unity (0.813-1.26). Thus, the decomposition of Ca acetate proceeds by means of the growth of reaction nuclei on the surface [16]. Log k decreased appreciably with a change in the material

of the vessel – it was less for quartz than for Pyrex. Dilution of the substance with an inert material (Al_2O_3) only insignificantly decreased log $\underline{k}$. Log $\underline{k}$ increased and $\underline{n}$ decreased with an increase in the amount of material from 0.57 to 1.14 and 1.7 mmoles. The decrease in $\underline{n}$ indicates an increase in the thermodynamic stability of the initial centers. Calculation of the activation energy gives considerably more realistic values than does calculation on the basis of the classical first order equation. Thus, E_{act} calculated from a graph plotting log $\underline{k}$ against $\frac{1}{T^\circ K}$ is 24 kcal/mole for experiments with the quartz crucible (1.7 mmole, sample), 29.6 kcal/mole for experiments with the Pyrex cup (1.14-mmole, sample), and 38 kcal/mole when 100 mg of Al_2O_3 was added (1.14-mmole, sample).

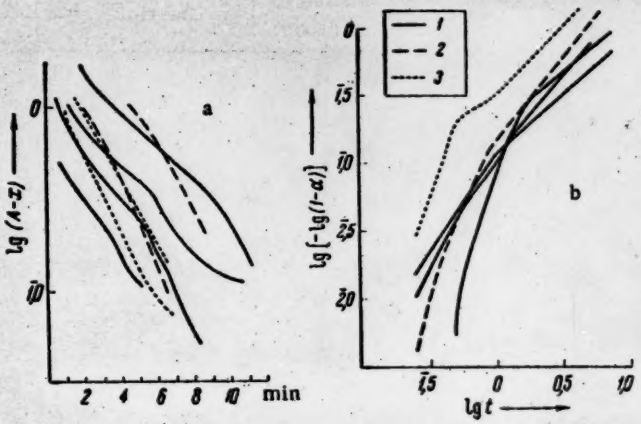


Fig. 3. Kinetic curves for the decomposition of calcium acetate under various conditions at 385-435°. a) In first order rate coordinates; b) in the Erofeev topokinetic equation coordinates. 1) In Pyrex; 2) in quartz; 3) in the presence of Al_2O_3.

The classical equation for a monomolecular reaction considerably more poorly described the kinetics of the decomposition of the acetate in all cases except for the experiments in which an inert material (Al_2O_3) was added. Evidently, in this case the catalytic action of the solid reaction product is suppressed by the Al_2O_3.

In conclusion, we note that additional experiments showed that irradiation of the sample with u. v. light during the reaction did not change the kinetics of the process.

LITERATURE CITED

[1] E. R. Squibb, J. Am. Chem. Soc. 17, 187 (1895); 18, 231 (1896).

[2] V. N. Ipatieff, J. Russ. Phys. Chem. Soc. 40, 514 (1908).

[3] V. D. Nefedov, M. A. Toropova, and I. A. Skul'skii, J. Phys. Chem. 29, 2236 (1955).

[4] E. Bamberger, Ber. 43, 3517 (1910).

[5] S. I. Kanevskaia, M. M. Shemiakin, and E. M. Bamdas, Ber. 67, 1518 (1934); 68, 257 (1935).

[6] E. M. Bamdas and M. M. Shemiakin, J. Gen. Chem. 18, 324 (1948).

[7] O. Neuenhoefer and P. Paschke, Ber. 72, 919 (1939).

[8] A. M. Rubinshtein and N. A. Pribytkova, Proc. Acad. Sci. USSR 78, 917 (1951).

[9] V. A. Komarov, Proc. Acad. Sci. USSR 87, 621 (1952); J. Phys. Chem. 27, 1748 (1953).

[10] M. I. Temkin and L. A. Shvartsman, Prog. Chem. 17, 259 (1948).

[11] F. D. Eastmen, J. Am. Chem. Soc. 45, 80 (1923).

[12] R. R. Wenner, Thermochemical Calculations,* (1950).

[13] W. Krönig, Z. angew. Chem. 37, 667 (1924).

[14] R. J. Read, J. Chem. Phys. 21, 377 (1953).

[15] B. V. Erofeev, Proc. Acad. Sci. USSR, 52, 515 (1946).

[16] P. I. Bel'kevich and B. V. Erofeev, Bull. Acad. Sci. BelorussSSR 1, 65 (1953).

N. D. Zelinskii Institute of Organic Chemistry

Received April 4, 1958

* In Russian.

INVESTIGATION OF THE KINETICS OF THE POLYMERIZATION OF ISOPRENE UNDER THE INFLUENCE OF A COMPLEX CATALYST

S. E. Bresler and M. I. Mosevitskii

(Presented by Academician V. A. Kargin, April 16, 1958)

Data on the kinetics of polymerization may be of great interest in clarifying the details of the mechanism of polymerization under the influence of complexes of organoaluminum compounds with titanium chlorides. The rate of polymerization of propylene has been studied previously [1, 2], but the interpretation of the kinetic data was difficult because the polymer proved to be practically insoluble in the reaction medium and coated the particles of the catalyst, as a result of which the rate of the process might depend on the diffusion of the monomer through the polymer to the active center.

In the present work we have investigated the polymerization of isoprene, which yields polymers soluble in the monomer, saturated hydrocarbons, and benzene. The rate of the polymerization reaction was measured by means of the thermal effect in a calorimeter that consisted of a Dewar flask (volume 3.5 liters) with a cover, placed in an air thermostat in which the temperature was maintained approximately equal to the reaction temperature. As the calorimetric liquid we used a spindle oil of low viscosity that was first heated to the reaction temperature (about 32°). The flask holder led to the outside and was connected to a shaking apparatus. The reaction flask was divided by a thin diaphragm into two spaces of 45-50 cc each. Into one of them were distilled the previously purified monomer and the solvent (total volume 35 cc); into the other were introduced the components of the catalyst from Schlenk vessels. The change in temperature in the calorimeter was determined with a Beckmann thermometer to an accuracy of 0.01°. After the temperature in the calorimeter containing the flask had been established (i.e., in 30-40 min) – it had not changed more than 0.01-0.02° – the shaking apparatus was turned on and a striker ruptured the partition. Vigorous shaking of the flask was continued during the whole experiment, so that both the contents of the flask and the calorimetric liquid were stirred. The reaction rate was determined from the rate of evolution of heat, i.e., from the rate of the temperature rise in the calorimeter. The reaction was practically isothermal, with a total temperature rise of 0.1-0.5°. Nevertheless, this rise was sufficient to make it possible to follow the course of the reaction with reasonable accuracy. It was confirmed by separate experiments that the calorimeter was adiabatic in character and that the mechanical sources of heat were negligible.

Figure 1 gives a series of kinetic curves for the polymerization of isoprene under the influence of titanium tetrachloride and triisobutylaluminum (ratio of catalyst components 1 : 1) with preliminary formation of the active complex in one of the compartments of the flask. First of all, let us note that the rate of polymerization was highest immediately after the addition of the monomer to the catalyst. An appreciable slowing down of the reaction occurred as a rule at rather low degrees of conversion (10-20%) and could not be explained by a decrease in the concentration of the monomer. It also was impossible to explain it by the coating of the particles of the catalyst by the polymer, since the polymer was soluble. The cause might be a chemical change in the surface of the catalyst or poisoning of it by secondary products of the polymerization reaction.

Unusual results were obtained when the catalyst components were introduced separately into the reaction mixture (one of the components was introduced with the monomer). In this case the course of the reaction was sharply changed. The first 30-40 min of the polymerization went very slowly, and the evolution of heat was practically unnoticeable. Moreover, some absorption of heat [connected, apparently, with the process of formation of the catalytic complex (Fig. 2)] took place during this period. After the induction period, an almost linear

increase in temperature started, accompanied by a corresponding accumulation of polymer. However, in this stage the polymerization proceeded more slowly than with the same amount of catalyst prepared beforehand. Another important fact should be noted: when the catalyst components were introduced separately, the reaction mixture was a clear, reddish-brown liquid which thickened as the reaction proceeded. Only a strong Tyndall effect, that developed when the flask was illuminated with a narrow beam of light, indicated that the catalyst was not dissolved in the medium, but formed a very finely dispersed colloid.

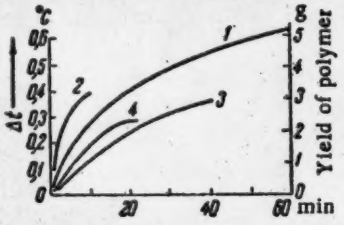


Fig. 1. Kinetic curves with introduction of the prepared catalyst into the reaction mixture. 1) Without solvent, 0.00012 mole of each catalyst component; 2) without solvent, 0.00048 mole catalyst component; 3) 50% solution in isopentane, 0.00012 mole of each catalyst component; 4) 50% solution in benzene, 0.00012 mole of each catalyst component.

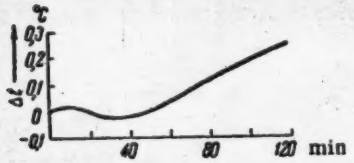


Fig. 2. Kinetic curve with introduction of triisobutylaluminum with the monomer. Polymerization without solvent; 0.00012 mole of each catalyst component.

The detailed interpretation of the characteristics of the polymerization when the catalyst components were introduced separately requires additional experiments; however, even now it is obvious that the reaction of the isoprene with the catalyst component introduced into it plays a significant role. In particular, the appearance of a yellowish coloration of the monomer when even a very small amount of $TiCl_4$ is introduced into it indicates the presence of a reaction. It would be wrong to assume that only the catalyst component first introduced into the monomer reacts with it; the second component also, which is in a separate compartment of the flask, apparently may react with the monomer after the rupture of the partition, since it is not yet bound in the complex.

Thus, the dissociation of the complexes of the catalyst components with the isoprene must procede the formation of the active complex. This process occurs in the presence of a considerable excess of the monomer and therefore takes an appreciable amount of time. The formation of the catalytic complex by itself is an exothermic reaction. However, in the case under consideration it is associated with the endothermic reaction of decomposition of the initial complexes of the catalyst components with the monomer, as a result of which the over-all reaction may prove to be even somewhat endothermic (Fig. 2).

In the light of what has been stated, the reason that the catalyst is in such a finely dispersed state when its components are introduced separately becomes apparent. Actually, with the usual means of formation of the catalyst in a small volume, many centers of crystallization are immediately formed which grow very vigorously and coalesce in a macroscopic precipitate. In this instance, however, as is clear from what has been said above, the process proceeds considerably more smoothly and in a larger volume. Here there is special significance in the fact that the formation of the catalyst takes place in the presence of the monomer. As soon as particles of active catalyst are formed, polymer molecules begin to grow in their surface, and to shield them from each other, hindering their further aggregation.

It is interesting to note that on polymerization of isoprene dissolved in benzene, previously prepared coarsely dispersed catalyst soon breaks down to colloidal dimensions, and the mixture outwardly becomes the same as when the catalyst components are introduced separately. Such a dispersing action of benzene is connected, apparently, with its complex-forming properties. In this instance the polymerization is sharply slowed down (Fig. 1, 4); this is in agreement with the general observation that the catalysts are less active when in the colloidal state.

Besides the kinetics, we have investigated (with I. Ia. Poddubnii and N. N. Chesnokova) the molecular-weight distribution of the polyisoprenes obtained by the action of the complex catalyst and separated out at various degrees of conversion [3]. It was established that the average molecular weights and the molecular-weight distributions within broad limits are practically independent of the degree of conversion. A hypothesis was expressed there regarding a mechanism of limitation of chain growth that leads to comparatively narrow and symmetrical molecular-weight distributions.

The authors express their thanks to N. N. Chesnokova for her help in the work.

LITERATURE CITED

[1] G. Natta, I. Pasquon, and E. Giachetti, Angew. Chem. 69, 213 (1957).

[2] G. Natta, I. Pasquon, and E. Giachetti, Macromol. Chem. 24, 3, 258 (1957).

[3] S. E. Bresler, M. I. Mosevitskii, I. Ia. Poddubnii, and N. N. Chesnokova, J. Tech. Phys. (USSR) 28, 11 (1958).

Institute of High Molecular Weight Compounds of the
Academy of Sciences, USSR

Received April 16, 1958

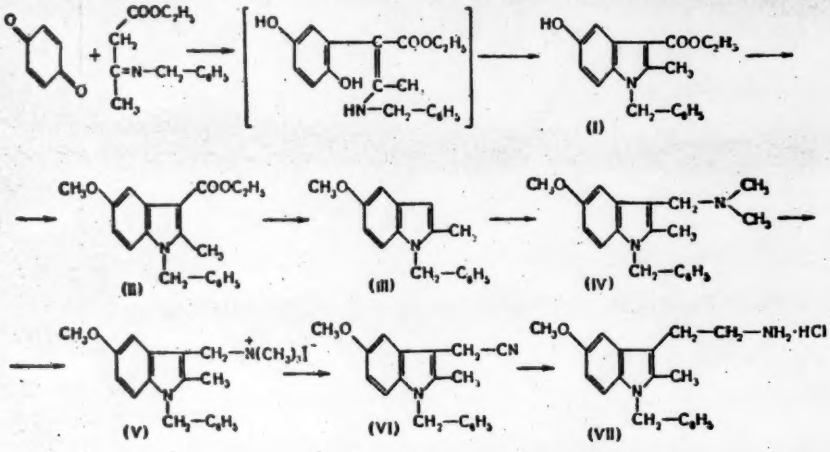
SYNTHESIS OF 1-BENZYL-2-METHYL-5-METHOXYTRYPTAMINE

A. N. Grinev, V. N. Ermakova, and Corresponding Member
AN SSSR, A. P. Terent'ev

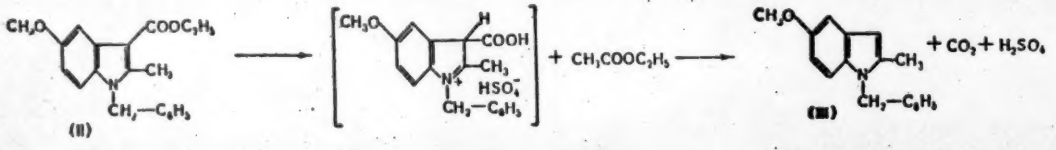
In 1955 Shaw [1] synthesized 1-benzyl-2-methyl-5-methoxyindolyl-3-acetic acid from the substituted phenylhydrazone of the methyl ester of levulinic acid by the Fischer reaction. By reduction of the amide of this acid with lithium aluminum hydride, 1-benzyl-2-methyl-5-methoxytryptamine was obtained.

As clinical experiments showed, the latter, which is the benzyl analog of serotonin (BAS), has a high physiological activity as an antimetabolite of serotonin [2-5].

In the present work a new synthesis of 1-benzyl-2-methyl-5-methoxytryptamine (VII) has been carried out by the following scheme:



The condensation of p-benzoquinone with the ethyl ester of N-benzyl-β-aminocrotonic acid to 1-benzyl-2-methyl-3-carboethoxy-5-hydroxyindole (I) could be brought about only under conditions differing from those for the preparation of the other 5-hydroxyindoles substituted on the nitrogen [6-9]. The methylation of the hydroxy group of the indole (I) proceeds smoothly under the action of dimethyl sulfate in an alkaline medium. The splitting out of the carboethoxy group from 1-benzyl-2-methyl-3-carboethoxy-5-methoxyindole (II) by the action of sulfuric acid in acetic acid solution proceeds most probably through a stage of the formation of an indolinine form:



The other stages of the process were carried out by methods similar to those described in [10, 11].

EXPERIMENTAL

1-Benzyl-2-methyl-3-carboethoxy-5-hydroxyindole (I). 34 g of p-benzoquinone was dissolved in 300 ml of dichloroethane. To the solution obtained was added 102 g of the ethyl ester of N-benzyl-β-aminocrotonic acid [12]. The reaction mixture was boiled in a distilling flask on a water bath for a half hour, during which time 220 ml of solvent distilled off. At the start of the reaction the dichloroethane distilled off together with water. The reaction mixture was cooled and the crystals of (I) were filtered off and washed with ether.

Yield 43 g (44%), m. p. 195° (from alcohol).

Found %: C 73.58, 73.66; H 6.28, 6.31. $C_{19}H_{19}O_3N$. Calculated %: C 73.76; H 6.19.

1-Benzyl-2-methyl-3-carboethoxy-5-methoxyindole (II). To a suspension of 70 g of the hydroxyindole (I) in 150 ml of dioxane was added 380 ml of 2 N sodium hydroxide, and then 75 ml of dimethyl sulfate. The reaction mixture was shaken for 40 minutes at room temperature, diluted with three volumes of water, and cooled. The crystals of (II) that separated out were filtered off.

Yield 63 g (86%), m. p. 102° (from methanol).

Found %: C 74.25, 74.12; H 6.61, 6.58. $C_{20}H_{21}O_3N$. Calculated %: C 74.28; H 6.55.

1-Benzyl-2-methyl-5-methoxyindole (III). To a solution of 30 g of (II) in 100 ml of acetic acid, heated to boiling in a flask with a reflux condenser, was added 30 ml of concentrated sulfuric acid in 50 ml of acetic acid. The reaction solution was heated to boiling for 15 minutes. The reaction mixture was cooled and neutralized, with cooling, with 2 N sodium hydroxide. The crystals of (III) were filtered off, washed with water, boiled in dioxane solution with carbon, and recrystallized from aqueous dioxane.

Yield 16 g (70%), m. p. 115.5-116°.

Found %: N 5.54, 5.52. $C_{17}H_{17}ON$. Calculated %: N 5.57.

1-Benzyl-2-methyl-3-dimethylaminomethyl-5-methoxyindole (IV). 19.4 g of dimethylamine hydrochloride as a 25% solution, 17 ml of formalin, and 30 g of (III) in 100 ml of dioxane were mixed with cooling. The suspension obtained was shaken for 4 hours at room temperature and left overnight. Isolation of the Mannich base (IV) was carried out in the usual manner.

Yield 30 g (80%), m. p. 83-84° (from aqueous dioxane).

Found %: N 8.89, 8.74. $C_{20}H_{24}ON_2$. Calculated %: N 9.08.

Methiodide of 1-benzyl-2-methyl-3-dimethylaminomethyl-5-methoxyindole (V). 30 g of (IV) was dissolved in 200 ml of absolute alcohol. To the solution obtained was added, with cooling, 6.7 g of methyl iodide. The reaction mixture was allowed to stand for 1 hour at room temperature. The crystals that separated out were filtered off and washed with absolute alcohol and ether.

Yield 40 g (93%), m. p. above 170° (with decomposition).

Found %: C 55.89, 56.06; H 6.14, 6.08. $C_{21}H_{27}ON_2I$. Calculated %: C 56.00; H 6.00.

Nitrile of 1-benzyl-2-methyl-5-methoxyindole-3-acetic acid (VI). To a solution of 7.2 g of sodium cyanide in 100 ml of water was added 27 g of (V) in 5 ml of dioxane. The solution that was formed was boiled for 2 hours, then cooled, and the crystals of (VI) that precipitated were filtered off.

Yield 23.2 g (90%), m. p. 128-129° (from toluene).

Found %: C 78.89, 78.83; H 6.40, 6.34. $C_{19}H_{18}ON_2$. Calculated %: C 78.59; H 6.25.

1-Benzyl-2-methyl-5-methoxytryptamine (VII). To a solution of 3 g of (VI) in 70 ml of absolute alcohol, heated to boiling, was added 1 g of finely cut sodium over a period of 5 minutes. The reaction mixture was heated to boiling until the sodium dissolved, diluted with one volume of water, and the alcohol was distilled off. The aqueous solution was extracted with a mixture of ether and benzene (50 ml of ether and 30 ml of benzene). From the ether-benzene layer the tryptamine (VII) was extracted with 1 N hydrochloric acid. The aqueous layer was concentrated until crystals precipitated, cooled, and the crystals were filtered off.

Yield of tryptamine hydrochloride (VII) 0.6 g (15%), m. p. 228-230° (from water). According to literature data, m. p. 230-231° [1].

Found %: C 68.67, 68.67; H 7.19, 7.00; N 8.56, 8.35. $C_{19}H_{23}ON_2Cl$. Calculated %: C 68.97; H 7.00; N 8.48.

LITERATURE CITED

[1] E. Shaw, J. Am. Chem. Soc. 77, 4319 (1955).

[2] D. Woolley and E. Shaw, J. Pharmacol. u. Exp. Therap. 116, 169 (1956).

[3] D. Woolley and E. Shaw, Circulation 16, 246 (1957).

[4] R. Wilkins, Engl. J. Med. 255, 185 (1956).

[5] A. Michelson and R. Wilkins, Science (Washington), 124, 34 (1956).

[6] A. N. Grinev, N. K. Kul'bovskaia, and A. P. Terent'ev, J. Gen. Chem. 25, 1355 (1955).*

[7] A. N. Grinev, V. I. Shvedov, and A. P. Terent'ev, J. Gen. Chem. 26, 1452 (1956). *

[8] A. N. Grinev, N. E. Rodzevich, and A. P. Terent'ev, J. Gen. Chem. 27, 1690 (1957). *

[9] A. N. Grinev, I. A. Zaitsev, V. I. Shvedov, and A. P. Terent'ev, J. Gen. Chem. 28, 446 (1958). *

[10] H. Snyder and E. Eliel, J. Am. Chem. Soc. 70, 1703 (1948).

[11] H. Kühn and O. Stein, Ber. 70, 567 (1937).

[12] R. Möhlau, Ber. 27, 3377 (1894).

M. V. Lomonosov
Moscow State University

Received March 21, 1958

* Original Russian pagination. See C. B. Translation.

CATALYTIC ALKYLATION OF n-BUTANE WITH ETHYLENE AT HIGH TEMPERATURES AND PRESSURES

N. M. Nazarova, Academician A. A. Balandin, and L. Kh. Freidlin

It has been established previously [1-3] that at elevated temperatures (450°) and pressures (500 atm) it is possible catalytically to alkylate normal paraffin hydrocarbons with olefins on aluminum oxide. At temperatures and pressures lower than this, propylene and butylene-1 are, for the most part, polymerized. Continuing the investigation in this direction, we have now studied the alkylation of butane with ethylene.

The experiments were carried out under circulating conditions; a diagram of the apparatus and the experimental and analytical methods were described in publication [1]. We used 90% ethylene (remainder ethane) and butane that contained 4.6% admixture of gaseous hydrocarbons. As catalysts aluminum oxide and aluminosilicate were used. The aluminum oxide, which was active in the dehydration of isopropyl alcohol, had the following characteristics: specific surface based on the adsorption of methyl alcohol (calculated by the BET method) 355 m^2/g, apparent density 0.89 g/cc, total volume of pores 0.86 cc/g. The aluminum oxide was impregnated with potassium difluoride (10% by weight of the Al_2O_3), treated with 50% sulfuric acid, and washed with water. Before the experiment the catalyst was calcined at 430° in a current of air.

The aluminosilicate was a commercial pelletized cracking catalyst with the following characteristics: specific surface 310 m^2/g; total volume of pores 0.69 cc/g; average pore radius 40 A; Al_2O_3 8.8 wt. %, SiO_2 88.3 wt. %.

The alkylates obtained were fractionated on a column with an efficiency of 70 theoretical plates.

The individual narrow fractions were freed of unsaturated materials by chromatographic separation on silica gel and were analyzed by their Raman spectra (KRS). The yield of alkylate was calculated on the ethylene taken for the reaction. The volumetric rate was expressed in liters of gas per liter of catalyst in 1 hour, and the yields of the individual fractions of the alkylate in volume percent.

The results of the experiments that were carried out show that in the reaction of butane with ethylene, as well as with propylene and butylene, a complex mixture of hydrocarbons is formed.

The expected hexane fraction – product of the addition of butane to ethylene – was larger than the other fractions of the alkylate, and its unsaturation was considerably less than that of the other fractions.

In Table 1 are given the experimental conditions, the yields of the alkylates, and the characteristics of the fractions obtained. In experiment No. 1 at 450°, 500 atm, and 15.7 wt. % of ethylene in the starting mixture with butane, the yield of alkylate was 84% and the degree of conversion of the ethylene was 82%. Approximately half of the alkylate (51.8 vol. %) distilled below 125°. The hexane fraction (b. p. 60-70°) was produced to the extent of 24.2%, about 50% of it passing over in the narrow fraction at 61-63°; the bromine number of the latter was 7.8 (see Fig. 1, I). In experiments Nos. 2 and 3, which were carried out on the same portion of catalyst and under similar conditions, but with a lower ethylene content in the mixture (9-10%), the yield of alkylate and the degree of conversion of the ethylene were somewhat less. However, 70% of the combined alkylate of these experiments distilled below 125°, and the content of the hexane fraction proved to be 37.3%; approximately 60% of it boiled at 62-63° (Fig. 1, II). The bromine number of this narrow fraction was 5.8. Upon distillation of the alkylates apart from the narrow 60-63° fraction, there also were separated narrow fractions

with b. p.'s 67-70° and 117-119°. In the fractionation curves I and II (Fig. 1) of the alkylates, the horizontal sections a and b correspond to them. In the combined alkylate of experiments Nos. 2 and 3, these fractions constituted 9 and 11 vol. %, respectively. By chromatographic separation on silica gel, all three narrow fractions

TABLE 1

Expt. No.	Exptl. conditions: Temp., °C	Pressure, atm.	ethylene content in mixt., wt. %	duration of expt., min	volume rate	Degree of conversion of ethylene, %	Yield of alkylate, wt. %	Characteristics of alkylates by fractions: < 60° yield, %	60–65° yield, %	60–65° bromine No.	65–70° yield, %	65–70° bromine No.	70–115° yield, %	70–115° bromine No.	115–120° yield, %	115–120° bromine No.
Catalyst – processed aluminum oxide																
1	450	500	15,7	280	1300	82	84	2,5	16,0	7	8,2	28	15,5	20	8,3	7
2	450	500	10,0	230	1500	77	75	3,0	28,0	6	9,3	30	10,3	57	14,5	24
3	450	500	9,3	170	1200	75	68									
4	450	300	10,6	65	1600	66	66	15,4	17,7	19	—	—	—	—	—	—
5	450	600	9,3	190	1000	76	87	7,5	19,5	26*	8,7	—	—	—	—	—
6	460	300	12,5	100	1200	74	81	7,3	26,5	15	12,6	38	—	—	—	—
7	450	200	12,5	290	1500	61	27	3,7	11,2	28*	8,2	—	—	—	—	—
Catalyst – unprocessed aluminum oxide																
8	450	450	12,1	160	550	81	135	5,2	29,0	8	10,8	30	12,2	48	7,2	21
9	450	300	11,0	160	1200	69	69	5,2	19,7	17	9,1	33	19,7	—	9,8	—
10	450	500	12,8	40	1000	75	—	—	—	—	—	—	—	—	—	—
11	450	300	12,0	240	850	65	103	6,8	21,2	15	8,3	43	13,0	23	7,6	25
Catalyst – aluminosilicate																
12	430	250	7,0	120	1500	52	30	Bromine number of alkylate 17								
13	450	500	10,2	110	1400	68	50	4,8	17,8	12*	6,2	—	16,3	—	14,4	—

* Bromine number determined for fraction 60-70°.

TABLE 2

B. p. °C	n_D^{20}	d_4^{20}	Spectrum frequencies, cm^{-1}	Hydrocarbon determined
60—63	1,3750	0,66284	442 (2); 736 (0); 750 (2); 766 (0); 816 (23); 879 (1); 952 (1*); 966 (1*); 989 (1*); 1018 (0); 1039 (2); 1050 (2); 1156 (1*); 1174 (1*); 1355 (0); 1447 (5); 1463 (5)	3-methylpentane
67—70	1,3755	0,6619	317 (0); 334 (0); 371 (1); 403 (0); 826 (2*); 871 (2); 893 (4); 901 (4); 1040 (4); 1082 (10); 1140 (1); 1305 (4); 1440 (7); 1460 (7)	n-hexane
116—119	1,3996	0,7101	454 (0); 745 (0); 762 (1); 821 (2); 874 (1); 905 (1); 961 (4); 978 (0); 1040 (1); 1064 (0); 1083 (0); 1147 (1); 1168 (1); 1222 (0); 1288 (0); 1302 (2); 1352 (1*); 1444 (7); 1464 (7).	3-methylpentane

were freed of unsaturated materials, and they were studied by the Raman spectrum method. In Table 2 are given the boiling points, n^{20}_D, d^{20}_4, and spectral frequencies of these fractions; according to the atlas of Raman spectra, the observed frequencies of these fractions correspond to the following respective content: 3-methylpentane, n-hexane, and 3-methylpentane. The values found for their n^{20}_D and d^{20}_4 also are close to those reported in [7]. In the Raman spectrum for the broad fraction 70-100°, which after separation from unsaturated materials had n^{20}_D 1.3915 and d^{20}_4 0.6927, frequencies were observed that corresponded to the spectrum of 3,3-dimethylpentane:

347 (1); 374 (1); 411 (1); 455 (1); 695 (5); 702 (2); 856 (1); 913 (1); 934 (1); 1005 (1); 1015 (10); 1057 (10); 1081 (1); 1196 (1 ш); 1220 (1); 1240 (1); 1447 (3); 1469 (2).

By analogy with thermal alkylation [4, 5] or with reactions in the presence of homogeneous catalysts [6] it might be expected that on a solid catalyst the reaction of butane with ethylene could be accomplished at a lower pressure than with propylene and butylene. The results of experiment Nos. 4 and 6 (Table 1) confirm this assumption. It is interesting to note that on a catalyst that had been working for some time, an alkylate was obtained with a higher content of the narrow fraction with b. p. 60-65°. Thus, in the alkylate of experiment No. 4, which was carried out in the presence of a fresh portion of catalyst, its content was 17.7 vol %, but in experiment No. 6 it was 26.5 vol. %.

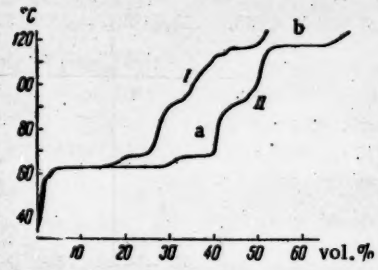


Fig. 1. Fractionation curves of alkylates: I) experiment No. 1, II) experiment Nos. 2 and 3.

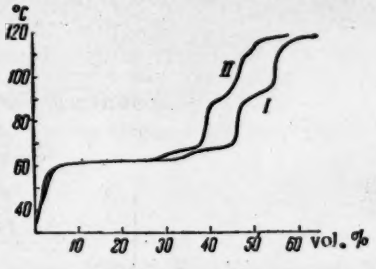


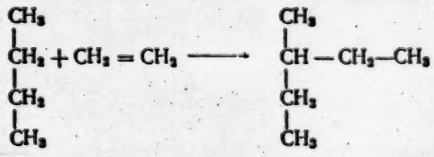
Fig. 2. Fractionation curves of alkylates: I) experiment No. 8, II) experiment No. 11.

When the pressure was lowered to 300 atm, the yield of alkylate was little changed, but the bromine number of the hexane fraction was increased somewhat.

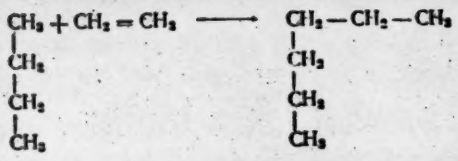
When the pressure was further lowered to 200 atm (experiment No. 7), there was a sharp decrease in both the yield of alkylate (to 27%) and the yield of the hexane fraction (to 11.2%).

Experiments Nos. 8-11 were carried out with aluminum oxide that had not been subjected to treatment with potassium difluoride. Analysis of the alkylates of experiments Nos. 8 and 11 (Table 1) and their fractionation curves (Fig. 2) shows that the yield of the alkylate and its fractional composition differed from those obtained in the presence of processed aluminum oxide.

From the experimental data obtained it follows that ethylene adds mainly to the second C atom of the butane, forming 3-methylpentane:



and to a lesser extent to the first C atom with the formation of n-hexane:



In the presence of an aluminosilicate catalyst, it also was possible to accomplish the reaction with ethylene at a lower pressure (250 atm) (experiment Nos. 12 and 13). The bromine number of the alkylate was small (Table 2), but the yield was low (approximately 30%). When the pressure was raised to 500 atm, the yield of alkylate was not substantially increased (50%).

In the alkylation process, besides the expected products there were higher-boiling hydrocarbons formed. It might be supposed that they are basically the product of multiple alkylation. In the reaction with ethylene there is an especially noticeable stage of realkylation of the 3-methylpentane that has been formed (Fig. 1, II). However, in this stage the addition goes predominantly on the first, and not on the second, C atom:

Comparison of the results of the present work with those previously obtained in the alkylation with propylene and butylene shows that the reaction of n-butane with ethylene goes according to the general scheme for all the hydrocarbons investigated by us, but at a lower pressure and with a higher yield of the expected fraction of hydrocarbons.

We express our thanks to Iu. P. Egorov and G. K. Gaivoronskaia for making and interpreting the spectra of the hydrocarbon fractions.

A. I. Palii and V. N. Zharov participated in the work.

LITERATURE CITED

[1] L. Kh. Freidlin, A. A. Balandin, and N. M. Nazarova, Proc. Acad. Sci. 96, 1011 (1954).

[2] L. Kh. Freidlin, A. A. Balandin, N. M. Nazarova, and Iu. P. Egorov, Proc. Acad. Sci. 105, 1270 (1955).

[3] L. Kh. Freidlin, A. A. Balandin, and N. M. Nazarova, Proc. Acad. Sci. 109, 1 (1956). *

[4] F. E. Frey and H. J. Hepp, Ind. and Eng. Chem. 28, 1439 (1936).

[5] C. C. Oberfell and F. E. Frey, Oil and Gas J. 38, 28, 50 (1939); 38, 29, 70 (1939).

[6] A. A. O'Kelly and A. N. Sachanen, Ind. and Eng. Chem. 38, 462 (1946).

[7] R. D. Obolentsev, Physical Constants of the Hydrocarbons of Liquid Fuels and Oils (1953). **

N. D. Zelinskii Institute of Organic Chemistry
of the Academy of Sciences, USSR

Received April 26, 1958

* Original Russian pagination. See C. B. Translation.
** In Russian.

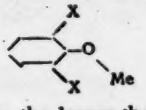
THE RELATION OF CONJUGATION CHARACTERISTICS TO THE ANGLE OF DEFLECTION OF THE METHOXYL AND THE DIMETHYLAMINO GROUPS RELATIVE TO THE PLANE OF THE BENZENE RING

P. P. Shorygin and Z. S. Egorova

(Presented by Academician B. A. Kazanskii April 11, 1958)

In the absence of steric hindrances, the indications of the reciprocal effect of the $-N(CH_3)_2$ or the $-OCH_3$ group and the benzene ring are easily observed. It is well known that the deviations from the data calculated by addition in the energy of the molecules of anisole and dimethylaniline determined from the heats of combustion amount to 8-10 cal/mole; the anomalies in the dipole moments of these molecules also are very considerable. Introduction of an $-OR$ and an $-NR_2$ group into the benzene ring leads to a significant drawing together and strengthening of the absorption bands, to a strong increase in the polarization of the molecule, and to a change in the other optical properties.

If we judge from the x-ray data, the methoxyl group in the absence of an ortho-substituent is located in the plane of the benzene ring. In the presence of a substituent (X) in molecules of the type



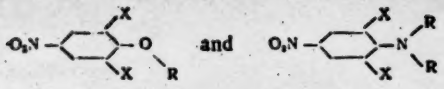
the location of the OMe group in the plane of the benzene ring becomes impossible; obviously, the larger the size of the group X, the greater must be the angle θ between the plane $C-O\diagdown C$ and the plane of the benzene ring.

The OH group is more compact than the OMe and therefore it should be comparatively little subject to the influence of steric factors.

The NMe_2 group of dimethylaniline obviously has a pyramidal configuration; the line joining the C atoms of the two methyl groups, apparently, is parallel to the plane of the benzene ring. In other compounds that contain electron-accepting groups (for example, in the molecules of nitroamines and some others) the NR_2 group may also have a planar configuration. Ortho-substituents should, naturally, disrupt the coplanarity of the system "benzene ring – dimethylamino group," but at the same time should have comparatively little effect on the more compact NH_2 group.

In the investigation of the influence of ortho-substituents (X) very great interest is afforded also by the X groups that have a large volume and at the same time have little direct effect on the benzene ring and on the benzene spectrum. From this point of view it was very desirable to study the tertiary butyl derivatives; unfortunately they were difficult to obtain. Among the halogen substituents the largest in size (bromine and iodine) substantially affect the benzene spectrum, causing a drawing together of the absorption bands; this makes it difficult to interpret the spectra of ortho-halogenated derivatives and to judge how much the effects of the OR and NR_2 groups are changed.

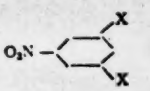
The difficulties in the interpretation of the spectra, which are connected with the direct effect of the X substituents on the benzene ring, become less substantial if we go to compounds of the type



It is known that p-nitrodimethylaniline has a very intense, sharp absorption band in the near-ultraviolet region, which is associated with the presence of the system of conjugated bonds of the "nitro group – benzene ring – amino group"; the same can be said of p-nitroanisole.

The indications of the effect of the NR_2 and OR on the "nitro group – benzene ring" system are expressed considerably more prominently than the indications of their effect on the benzene ring in the $PhNR_2$ and PhOR molecules.

The presence of the nitro group also makes it possible to obtain supplementary criteria for judging the effect of NR_2 and OR groups at different angles of deflection (θ) on the system of conjugated bonds: the frequency of the valence vibration of the nitro group observed in the Raman spectra can be used as an approximate measure of changes in the rigidity of the N–O bonds that are caused by the substituents located in the para-position, i.e., the NR_2 or OR groups. The intensity of the nitro group line is especially sensitive to the influence of such substituents.

At the same time the substituents X in the compounds  have comparatively little effect on the absorption spectra and on the frequency of the nitro group, and the dipole moments of such compounds are additive.

In Table 1 the following data are given for each compound:

1) the difference ($\Delta\omega$) between the frequency of the symmetrical valence vibration of the nitro group of the given compound and the frequency of unsubstituted nitrobenzene (1347.3 cm^{-1}) according to Raman spectrum measurements of benzene solutions; 2) the coefficient of integral intensity of the corresponding line of the nitro group, I_{NO_2}, from measurements of benzene solutions; the coefficient of intensity of the benzene line 1176 cm^{-1} is taken as 25 units (as a unit we used 1/100 of the integral intensity of the line 313 cm^{-1} of CCl_4 calculated for 1 mole); accuracy ± 15%;* 3) the dipole moment from measurements in benzene, μ in Debyes (figures with the letter *l* in the list are taken from the literature); 4) the difference ($\Delta\mu$) between μ and the vectorial sum of the dipole moments of nitrobenzene (or, respectively, m,m-dichloronitrobenzene for the dichloro derivatives) and the aliphatic compound Al kZ (where Z = OH, OR**, NH_2, or NR_2); roughly speaking, $\Delta\mu$ characterizes the shift of electrons from Z toward the benzene ring and the nitro group; by calculating $\Delta\mu$ the deformation of the C–C–Cl angles and others are learned (an approximate estimate); 5) the values of θ (angle of deflection of the NH_2, NR_2, OH, or OR group around the C_{ar}–N or C_{ar}–O bond) calculated from known data on the interatomic distances in similar molecules and the van der Waals radii of the H and Cl atoms. In the calculation we took into account the deformation of the valence angles and the drawing together of the adjacent H and Cl atoms to a distance less than the sum of their van der Waals radii under the influence of the force striving to turn the NR_2 group (or OR) into the plane

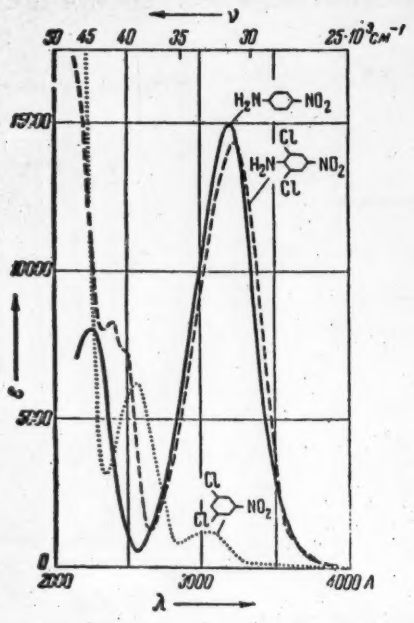


Fig. 1

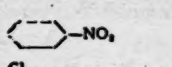
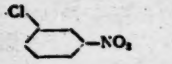
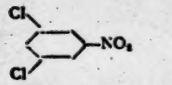
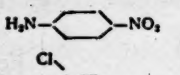
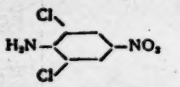
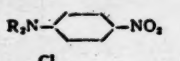
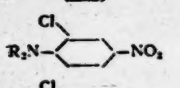
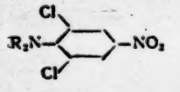
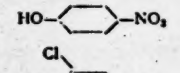
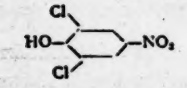
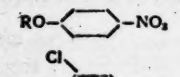
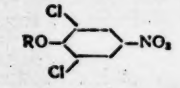
* Excitation from Hg 4358 A. Details of measurements of ω, I, μ, are given in [1].

** In text and in Table 1 the letter R indicates the methyl group.

of the benzene ring. According to an approximate estimate this force should be about $5 \cdot 10^{-5}$ dyne. Such a force is sufficient to reduce the distance between the adjacent atoms by 0.1 - 0.2 A. For the calculation the form of the $-NR_2$ group was assumed to be planar.

According to the data of Table 1, the OH, OR, NH_2, and NR_2 groups in the molecules of p-nitrophenol, p-nitroanisole, p-nitroaniline, and p-nitrodimethylaniline have the effect of lowering the frequency of the nitro group, increasing the intensity of the Raman line of the nitro group, and strengthening and drawing together the absorption bands. Anomalies in the dipole moments are particularly great in the nitroamines.

TABLE 1

	$\Delta\omega_{NO_2}$	I_{NO_2}	UV absorption spectra in pentane	μ	$\Delta\mu$	θ
	0	700	2800 (1,5) 2520 (9,6)	4,00[l]	0	—
	1,5	600	2900 (1,2) 2520 (7,4)	3,40[l]	—0,1	—
	0	500	3070 (1,2) 2570 (6,2)	2,55[l]	0,1	—
	—12	20000	3190 (15) 2260 (8)	6,20[l]	1,8	0°
	—13	18000	3220 (14,4) 2400 (8)	4,87	1,8	0°
	—28	200000	3540 (20) 2260 (8)	6,87[l]	2,8	0°
	—16	~100000	3450 (12) ~ 2200	5,50	1,8	~55°
	—12	~90000	3650 (7,5) 2590 (5)	4,05	1,4	~65°
	—5	3000	2850 (10,5)	5,01[l]	1,4	0°
	—5	2000	2850 (6,5)	3,30	1,2	0°
	—5	4000	2920 (12)	4,90[l]	1,4	0°
	—2,5	1300	2720 (8,4)	3,42	1,2	~60°

* Figures in parentheses are $\epsilon_{max} \cdot 10^{-3}$.

Comparison of the data for 4-nitrophenol and 2,6-dichloro-4-nitrophenol shows that in the spectra of the latter clear indications of the weakening of the effect of the OH group on the system "benzene ring — nitro group" were not observed; the intensity of the absorption band (and also I_{NO_2}) in this compound was somewhat lowered, but to approximately the same extent as in m,m-dichloronitrobenzene in comparison with nitrobenzene. It can be assumed that the orientation of the OH group (angle θ) is not substantially changed as a result of chlorination.

The methyl group is less compact than the OH and should be more subject to the influence of steric factors. Actually, when an atom of chlorine was introduced into the molecule of p-nitroanisole, a clear weakening of the effect of the OR on the spectra was observed. However, the value of $\Delta\mu$ was decreased insignificantly (approximately the same as for the analogous phenol). Whether this is explained by an inaccuracy in the value obtained for μ or by other circumstances is not clear as yet.

Thus, the indications of the influence of the OR group on the spectra depend on the angle θ and are weakened as it increases; a relationship of $\Delta\mu$ to θ has not been detected here.

Comparison of the parameters of the molecules of 4-nitroaniline and 2,6-dichloro-4-nitroaniline shows that the chlorine atom has very little effect on the spectra and on the indications of the influence of the NH_2 group on the system "benzene ring – nitro group" observed in the spectra and dipole moments (see Fig. 1 for absorption spectra).

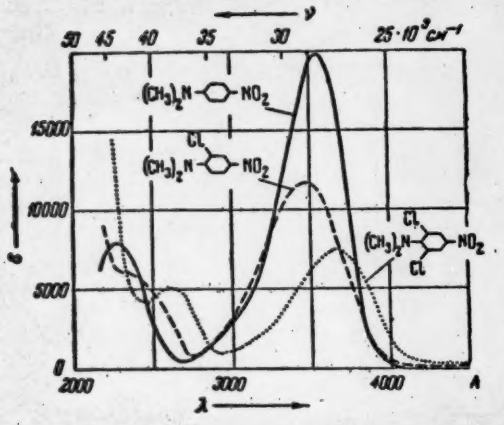


Fig. 2

An entirely different picture is observed when atoms of chlorine are introduced into the p-nitrodimethylaniline molecule: even when one chlorine atom is introduced, the indications of the influence of the NR_2 group on the system of conjugated π-bonds are clearly weakened; two chlorine atoms give a still greater effect: the frequency of the NO_2 group becomes closer to the frequency of unsubstituted nitrobenzene than to the frequency of the starting p-nitrodimethylaniline; the intensity of the line for the nitro group (I_{NO_2}) is weakened by half, the absorption band is weakened still more (see Fig. 2), and the anomalies in the dipole moments ($\Delta\mu$) are decreased by half.

It is obvious that the effect of the NR_2 group on the spectra and the dipole moments of aromatic compounds is greatly dependent on the angle of deflection θ of this group relative to the plane of the benzene ring; when θ is increased from 0 to 60° the indications of the influence of the NR_2 group are weakened, roughly speaking, by half (it should be noted that deflection of the nitro group by an angle of about 60° [2] leads to a more distinct weakening of the indications of conjugation of the nitro group with the benzene ring).

Unfortunately, at present data are lacking for molecules in which the angle θ is close to 90°. However, data already available permit the assumption that an inductive effect is not the factor determining the anomalies in the spectra and the dipole moments of molecules in which the NR_2 group is linked to a system of π-bonds.

LITERATURE CITED

[1] P. P. Shorygin and Z. S. Egorova, J. Phys. Chem. 32, 4 (1958).

[2] P. P. Shorygin and Z. F. Il'icheva, Proc. 9th All-Union Conf. on Spectroscopy (Moscow, 1957).*

L. Ia. Karpov Scientific-Research
Physico-Chemical Institute

Received April 4, 1958

* In Russian.

HYDROCARBONS OF THE DECALIN SERIES IN MIRZAANI PETROLEUM

Kh. I. Areshidze and A. V. Kikbidze

(Presented by Academician B. A. Kazanskii, April 24, 1958)

The thorough investigation of the chemical composition of the petroleum fractions with b. p. above 150° is one of the timely and most important problems of petroleum chemistry.

We have shown that the fraction of Mirzaani petroleum boiling at 150-200° contains 23.6% of hydroaromatic hydrocarbons. It was of interest to determine the individual nature of these hydrocarbons, and the present investigation was devoted to this study. The interest in establishing the structure of the hydroaromatic hydrocarbons of the decalin series in Mirzaani petroleum was redoubled by the fact that in this same petroleum we found naphthalene, α- and β-methylnaphthalene, and 1,6-dimethylnaphthalene of the condensed aromatic hydrocarbons.

It was of definite interest to show whether the presence of the condensed aromatic hydrocarbons found in earlier investigations [1, 2] and of their hydrogenated analogs was characteristic only of Surakhany oily petroleum or could also characterize other petroleums.

The investigation that was carried out showed that condensed aromatic hydrocarbons and their hydrogenated analogs were present in Mirzaani petroleum.

The accumulation of much experimental material provided a basis for confirming a possible genetic connection between the condensed aromatic hydrocarbons and their hydrogenated analogs.

As a result of the investigation carried out we have shown that decalin, α-methyldecalin, and 1,6- and 1,7-dimethyldecalin are present in Mirzaani petroleum.

A study of the naphthenic hydrocarbons in the kerosene of various petroleums of the Soviet Union, and primarily of their content of decalin and its homologs, was carried out in the S. S. Nametkin laboratory of the Institute of Petroleum of the Academy of Sciences of the USSR.

L. M. Rozenberg [2] investigated the hydrocarbons of the decalin series in the kerosene of Surakhany (oily) petroleum by catalytic dehydrogenation and the picrate method and established that decalin, a mixture of α- and β-methyldecalins, and 1,6-dimethyldecalin were present in it. L. M. Rozenberg and S. S. Nifontova [3] by the same methods established the presence in kerosene of Kossor petroleum of the same hydrocarbons as in the kerosene of Surakhany (oily) petroleum, with the exception of decalin.

The object of investigation in the present work was the 150-200° fraction of an average sample of Mirzaani petroleum, which was isolated from the petroleum by fractional distillation.

In order to remove the nonhydrocarbon components entering into the 150-200° fraction of Mirzaani petroleum, we treated it with 75% sulfuric acid, after which it was washed, dried, and distilled from a Favorskii flask in the presence of metallic sodium.

The maximum aniline point, the refractive index, and the specific gravity were determined for the 150-200° fraction investigated, the values of which are given in Table 1.

Separation of the aromatic hydrocarbons entering into the composition of the fraction investigated was accomplished by chromatographic adsorption on "KSM"-brand silica gel. The active fraction was 100-200 mesh and had an activity, relative to benzene, of 13.5.

The completeness of dearomatization was verified by the method of A. M. Nastiukov [4]. The same physical properties were determined for the dearomatized fraction, after it had been appropriately washed, dried, and distilled, as before the removal of the aromatic hydrocarbons, and the values are given in Table 1.

TABLE 1
Properties of 150-200° Fraction of Mirzaani Petroleum Before and After Catalysis

	Maximum aniline point		$n^{20}D$		d^{20}_4	
	before catalysis	after catalysis	before catalysis	after catalysis	before catalysis	after catalysis
Before removal of aromatic hydrocarbons	58.4	46.4	1.4363	1.4432	0.7810	0.7900
After removal of aromatic hydrocarbons	68.4	71.3	1.4210	1.4018	0.7593	0.7514

To establish the nature of the naphthenic hydrocarbons, the dearomatized petroleum was subjected to dehydrogenation on platinized carbon (Pt 10%), containing iron for the purpose of suppressing the hydrogenolysis of the cyclopentane hydrocarbons as had been indicated by B. A. Kazanskii and G. S. Landsberg [5]. The dehydrogenating capacity of the catalyst was checked by the method of G. S. Pavlov. The catalyst converted 95% of cyclohexane to benzene.

The aromatic hydrocarbons that were formed as a result of the dehydrogenation of the hydroaromatic hydrocarbons were removed by the same method as the aromatic hydrocarbons of the benzine from the direct distillation. The same constants were determined for the catalyzate before and after removal of the aromatic hydrocarbons (Table 1).

From the depression of the aniline points with the use of the proper factors we calculated the group composition of the fraction under investigation (in percent): aromatic 15.1; hydroaromatic 23.6; other cyclanes 27.3; paraffins 34.0. Percent of hydroaromatics in total amount of cyclanes – 46.3.

The aromatic hydrocarbons that were formed as a result of catalysis were separated by chromatographic adsorption, washed, dried, and distilled from a Favorskii flask in the presence of metallic sodium; the properties and amount of the fractions of aromatic hydrocarbons collected are given in Table 2.

TABLE 2
Properties and Amount of Fractions of Aromatic Hydrocarbons Isolated from the Catalyzate of the 150-200° Fraction of Mirzaani Petroleum

Fraction No.	B. p. °C (736 mm Hg)	n_D^{20}	d_4^{20}	Amount of fraction, g
1	135—155	1,4792	0,8321	15
2	155—175	1,4860	0,8421	17
3	175—195	1,4930	0,8643	20
4	195—220	1,5140	0,9319	20

The fractions of aromatic hydrocarbons were treated separately with picric acid to isolate the condensed aromatic hydrocarbons.

From the 135-155° and the 155-175° fractions pure picric acid precipitated. Both precipitates after crystallization melted at 122-123° and gave no depression with picric acid, from which it follows that they contained neither naphthalene nor its homologs.

From the 175-195° fraction a picrate was obtained which, after several recrystallizations from ethyl alcohol yielded two picrates: one formed needle-like crystals of an orange-yellow color with m. p. 141°, which agrees with the m. p. of the picrate of α-methylnaphthalene. According to the literature [6], the m. p. of the picrate of α-methylnaphthalene is 141°. The second formed yellow crystals that melted at 149° and agreed with the m. p. of the picrate of naphthalene. In the lit rature the m. p. 149.5° is given for the picrate of naphthalene [7].

A picrate was obtained from the 195-220° fraction; two distinct picrates were isolated from this after several recrystallizations from ethyl alcohol: one was bright orange in color, with m. p. 111-112°, which according to the literature agrees with the picrate of 1,6-dimethylnaphthalene [8]. The second, which melted at 120-121°, corresponded to the picrate of 1,7-dimethylnaphthalene [8].

On the basis of the picrates isolated we have established the presence of decalin, α-methyldecalin, 1,6- and 1,7-dimethyldecalins in Mirzaani petroleum.

LITERATURE CITED

[1] S. S. Nametkin, E. S. Pokrovskaia, and T. G. Stepantseva, Proc. Acad. Sci. 67, 847 (1949).

[2] L. M. Rozenberg, Proc. Acad. Sci. 80, 769 (1951).

[3] L. M. Rozenberg and S. S. Nifontova, Third All-Union Conf. on Chemistry and Processing of Petroleum,* Baku, 1953, p. 136.

[4] A. M. Nestiukov, J. Russ. Chem. Soc. 36, 881 (1904).

[5] G. S. Landsberg and B. A. Kazanskii, Bull. Acad. Sci. USSR, Div. Chem. Sci. (1951), 100.

[6] S. H. Morrell, J. B. Pickering, and J. C. Smith, J. Inst. Petr., 34, 677 (1948).

[7] F. K. Beilstein, Handb. d. org. Chem. Erg. 11, 5, 144 (1943).

[8] A. S. Beiley, K. C. Bruyant et al., J. Inst. Petr. Techn. 34, 677 (1948).

P. G. Melikishvila Institute of Chemistry
of the Academy of Sciences, USSR

Received April 24, 1958

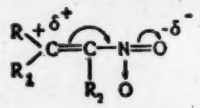
* In Russian.

INVESTIGATION OF THE STRUCTURE OF UNSATURATED NITRO COMPOUNDS BY MEANS OF THEIR RAMAN SPECTRA

Ia. S. Bobovich and V. V. Perekalin

(Presented by Academician A. N. Tereninyi, April 14, 1958)

It has been shown by numerous investigations that for the successful reaction of unsaturated nitro compounds with nucleophilic reagents, and in particular with compounds with labile hydrogen atoms in the methyl and methylene groups, the presence of an electron deficiency (δ+) on the carbon atom of the ethylene group of the nitroolefin is of decisive importance. The magnitude of the electron deficiency, which is conditioned by the conjugation of the nitro group with the double bond, depends substantially on the chemical structure of the unsaturated compounds (the nature of the radicals linked with the ethylene group).



where R = H, alkyl, aryl, heterocycle; R_1, R_2 = H, alkyl, aryl.

For the solution of a number of synthetic problems, the necessity arose for satisfactory objective information on the character of the conjugation in nitroolefins. For this purpose, the intensities of the bands of the Raman series (XXII) for unsaturated nitro compounds, nitromethane, and several aromatic nitro derivatives were investigated. The spectra of the majority of these compounds were obtained for the first time.

As is well known [1], the intensities of the Raman lines, changing sharply in dependence upon the conjugation, can be employed for its evaluation. Furthermore, the Raman lines, being characteristic, in the absence of ultraviolet absorption bands permit judgment of local changes in the electron density, but not of the behavior of the molecule as a whole.

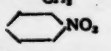
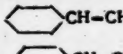
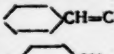
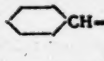
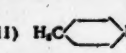
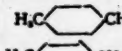
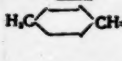
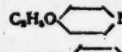
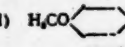
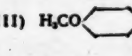
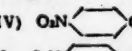
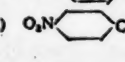
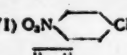
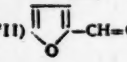
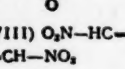
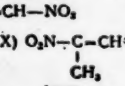
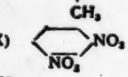
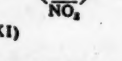
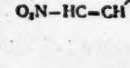
The investigations were carried out by means of photoelectric equipment. Acetone served as the solvent in all cases. The concentrations of the materials varied within the range 10^{-1} to 10^{-3} moles/liter, which practically excluded the possibility of reaction of the molecules of the substances investigated. The precision of reproducibility of the results for the intensities lay within the limits ± 3-4% and for the frequencies was ±5 cm^{-1}. The intensities and frequencies were measured for the lines of fully symmetrical and antisymmetrical vibrations of the nitro group, antisymmetrical vibration of the benzene ring, and vibrations of the double bond. For this purpose, the measure of the intensity of the lines was its ratio to the intensity of the 1707 cm^{-1} line of acetone. For nine compounds quantitative polarization measurements also were made. All the data on frequencies and intensities, reduced to an identical concentration of the compounds and to the same number of nitro groups and double bonds, and on the state of polarization of the lines, are assembled in Table 1.

The investigation that was carried out showed that the intensities of the lines varied within very wide limits (Table 2). For the same molecules the intensities of the antisymmetrical vibration of the benzene ring were subject to especially severe variations.

The changes in the intensities of the lines of the Raman spectra of the nitro group, the double bond, and the aromatic ring directly reflect their participation in the π-electron reaction, presenting a clear representation of the relationship of conjugation in the nitroolefins to their structure, and permit the following conclusions.

TABLE 1

Frequencies (in cm^{-1}), Intensities (on an arbitrary unit scale), and Degrees of Depolarization of Some Raman Lines in the Spectra of Styrene and Nitro Compounds

Formula	Fully symmetrical vibration of the NO_2 group	Antisymmetrical vibration of the NO_2 group	Antisymmetrical vibration of the ring	Vibration of the double bond C = C
(I) CH_3NO_2	1380+1400 (0,02; $\rho = 0,32$)	1555 (0,005 $\rho = 0,74$)	—	—
(II) $CH_3CH_2CH_2CH{=}CH{-}NO_2$	1340 (0,36)	1510 (0,054)	—	1650 (0,187)
(III) $CH_3CHCH{=}CH{-}NO_2$ (CH$_3$)	1340 (0,38)	1510 (0,042)	—	1650 (0,183)
(IV) 	1345 (0,75; $\rho = 0,22$)	1510 (0,04; $\rho = 0,72$)	1600 (0,16; $\rho = 0,55$)	—
(V) 	—	—	1610 (0,3, ρ=0,55)	1640 (0,42; $\rho = 0,28$)
(VI) 	1320 (9; $\rho = 0,32$)	?	1600 (2,4 $\rho = 0,43$)	1630 (4,3, $\rho = 0,35$)
(VII) 	1325 (4,3)	?	1600 (1,3)	1660 (2,3)
(VIII) 	1340 (1,5; $\rho = 0,32$)	?	1600 (0,41)	—
(IX) 	1335 (10,6)	1510 (0,9)	1620 (4,1)	1640 (4,2)
(X) 	1320 (7,3)	?	1615 (2,6)	1660 (3,7)
(XI) 	1340 (5; $\rho = 0,42$)	1500 (0,2, $\rho = 0,50$)	1600 (1; $\rho = 0,50$)	—
(XII) 	1325 (40; $\rho = 0,39$)	1500 (3,7)	1600 (19; $\rho = 0,38$)	1625 (10; $\rho = 0,30$)
(XIII) 	1305 (26)	?	1590 (10)	1640 (10)
(XIV) 	1335 (3,4)	1510 (0,45)	1590 (4,1)	1630 (4,8)
(XV) 	1345 (2,8)	?	1600 (3)	1665 (3)
(XVI) 	1340 (30)	?	1590 (39)	1630 (27)
(XVII) 	1335 (255)	?	—	1620 (95)
(XVIII) 	1335 (16; $\rho = 0,36$)	1510 (2,8)	1610 (50; $\rho = 0,41$)	1625 (18; $\rho = 0,39$)
(XIX) 	1325 (14; $\rho = 0,43$)	1515 (0,7)	1610 (25; $\rho = 0,49$)	1660 (11; $\rho = 0,43$)
(XX) 	1340 (0,4)	1520 (0,13)	1595 (0,14)	—
(XXI) 	1340 (8)	1510 (1,0)	1595 (3,56)	1630 (5,4)
(XXII) 	1325 (3,5)	1510 (0,20)	1610 (1,3)	1665 (2,8)

1. The unsaturated olefins represent a single conjugated system: in the aliphatic nitroolefins the nitro group is conjugated with the double bond, but in the aromatic compounds the nitro groups, double bond, and benzene ring are involved, as is revealed in a still sharper increase in the intensity of the spectral lines in comparison with compounds that do not contain these three groups simultaneously. Nucleophilic substituents in the para-position of the benzene ring (methyl and methoxyl groups) are conducive to conjugation in exactly the same way as in the case of the aromatic nitro compounds according to the data of P. P. Shorygin [1].

TABLE 2

Character of vibration	Compounds compared	Change in intensity (number of times)
Fully symmetrical vibration of nitro group	(I) and (XII)	2000
Antisymmetrical vibration of benzene ring	(IV) and (XVIII)	~312
Vibration of double bond	(II) and (XVIII)	~ 98

2. In the para-dinitroolefins (XVIII) and (XIX) the conjugation increases sharply in comparison with the corresponding meta-isomers (XXI) and (XXII) and the mononitroolefins (VI) and (VII), although in (XVIII) and (XIX) it would be expected that there would be a weakening of the lines as a result of the presence in the molecules of oppositely directed conjugated systems.

3. Methyl groups on the ethylene carbon linked with the nitro group weaken the conjugation, apparently as a result of disturbance of the coplanarity of the molecule (compare the intensities of the bands of the nitro group, benzene ring, and double bond in the compounds (VI), (IX), (XII), (XIV), with those in (VII), (X), (XIII), and (XV), respectively.

4. The degree of depolarization of the fully symmetrical vibration of the nitro group in conformity with the earlier observations by one of us [2] is included for the majority of the compounds within the limits 0.22-0.43. Comparison between compounds XII and XI, for which $I_1 = 40$, $\rho_1 = 0.39$ and $I_2 = 5$, $\rho_2 = 0.42$, respectively, indicates that introduction into the chain of a double carbon-carbon bond leads not to a simple elongation of one of the axes of the ellipsoid $\frac{\partial \alpha}{\partial q}$ of the nitro groups, but to simultaneous elongation of all of its axes, i.e., to a substantial change in the form of the ellipsoid. In molecules characterized by favorable conditions for conjugation, the line for the vibration of the benzene ring becomes distinctly polarized (in the case of compound (XII) the degree of depolarization of this line is 0.38). This last fact, it would seem, indicates a change in the form of the "antisymmetrical" vibration of the benzene as a result of the conjugation of the bonds.

The authors express deep gratitude to Academician A. N. Terenin and Professor B. S. Neporent for their interest in the work and for presenting the opportunity to carry out the spectroscopic portion of the investigation.

LITERATURE CITED

[1] P. P. Shorygin, Doctor's Dissertation, L. Ia. Karpov Phys.-Chem. Inst. (Moscow, 1949). *

[2] Ia. S. Bobovich and M. V. Vol'kenshtein, Proc. Acad. Sci. 71, 1045 (1950).

Received April 2, 1958

* In Russian.

DIPOLE MOMENTS OF HEXAALKYL DERIVATIVES OF DISILOXANE

A. A. Gundyrev, N. S. Nametkin, and Academician A. V. Topchiev

In the present communication values are presented for the dipole moments of four hexaalkyl derivatives of disiloxane: hexamethyldisiloxane, hexaethyldisiloxane, hexapropyldisiloxane, and hexabutyldisiloxane, obtained by the hydrolysis of the corresponding trialkyl halide (ethoxy) of the silanes [1].

The dipole moment of hexamethyldisiloxane has been determined by a number of authors [2, 3], while the dipole moments of the other hexaalkyl derivatives of disiloxane were measured for the first time by us. The dipole moments were calculated by us from the magnitude of the dielectric constants of dilute solutions of these compounds in a nonpolar solvent, n-hexane.

The dielectric constants were measured in an apparatus operating by a pulsating method. The instrument was stabilized by a piezo quartz crystal with a frequency of $7.59 \cdot 10^5$ hertz. The measuring condenser consisted of three concentric platinum cylinders. The outer and inner cylinders were connected to each other in several places by platinum wire and this electrode was grounded, so that the middle electrode was shielded.

The interelectrode capacity of this condenser proved to be 12,363 pF for measurements in benzene. Using this figure and the results of the experimental data from the measurement of the capacity of this condenser filled with the compound, we calculated the dielectric constant of toluene, n-hexane, and hexamethyldisiloxane at 25°. The values obtained and the literature data are given in Table 1.

TABLE 1
Dielectric Constants of Toluene, n-Hexane, and Hexamethyldisiloxane at 25°.

Compound	Our data (ε_1)	Lit. data (ε_2)	$\frac{\varepsilon_1-\varepsilon_2}{\varepsilon_2} \cdot 100$
Toluene	2,3744	2,3738 (4)	+0,03
n-Hexane	1,8854	1,8867 (5)	—0,07
Hexamethyldisiloxane	2,1719	2,17* (6)	—

* for T = 20°.

Comparison of these data shows the very high precision of the instrument.

Measurement of the dielectric constant ϵ, the d density $\underline{d}$, and the refractive index n_D was carried out at 25 ± 0.05°. The dielectric constant was determined with an accuracy of 0.02%. The density of the solutions was determined with a pycnometer with an accuracy of 0.02% and the refractive index in an IRF-23 refractometer with an accuracy of 0.01%.

The dipole moments of the hexaalkyl derivatives of disiloxane were calculated by the method of Hederstrand [7] according to the formula:

$$\mu = 0{,}012813 \cdot 10^{-18} \sqrt{P_{op} T} \qquad (1)$$

where μ is the dipole moment, P_{op} is the orientation polarization, and T is the absolute temperature.

The orientation polarization is associated with the total polarization of the dissolved material P_∞ and the deformation polarization $P_{D\infty}$, assumed to be equal to the molar refraction, by the following relationship:

$$P_{op} = P_\infty - P_{D\infty}. \qquad (2)$$

The designation ∞ indicates that the values P_∞ and $P_{D\infty}$ are extrapolated to infinite dilution by the method of Hederstrand.

The total polarization at infinite dilution was calculated by the following formulas, in which the designation 1 refers to the pure solvent and the designation 2 refers to the dissolved material; the dielectric constant ϵ, the density $\underline{d}$, and the refractive index n_D without subscripts are the values characteristic of the solution; C_2 is the mole fraction of the dissolved substance, and M_1 and M_2 are the molecular weights of the solvent and the dissolved material, respectively.

The total polarization of the dissolved material is:

$$P_\infty = A\left(M_2 - \beta d_1 \frac{M_1}{d_1}\right) + B\alpha\varepsilon_1, \tag{3}$$

where

$$A = \frac{\varepsilon_1 - 1}{\varepsilon_2 + 2}\frac{1}{d_1}, \quad B = \frac{3M_1}{d_1(\varepsilon_1 + 2)^2} \quad \beta d_1 = \frac{d - d_1}{c_2} \text{ and } \alpha\varepsilon_1 = \frac{\varepsilon - \varepsilon_1}{c_2}.$$

The deformation polarization of the dissolved material is:

$$P_{D_\infty} = A'\left(M_2 - 3d_1\frac{M_1}{d_1}\right) + B'\gamma n_1^2, \tag{4}$$

(4)

where

$$A' = \frac{n_1^2 - 1}{n_1^2 + 2}\frac{1}{d_1}; \quad B' = \frac{3M_1}{d_1(n_1^2 + 2)^2}$$

$$\text{and } \gamma n_1^2 = \frac{n^2 - n_1^2}{c_2}.$$

In Table 2 are given the constants for the pure solvent for the calculation of P_∞ and $P_{D\infty}$.

TABLE 2

Constants of n-Hexane

Constants for calculation of P_∞					
M_1	d_4^{25}	ε_{25}	$\frac{M_1}{d_1}$	A	B
86,18	0,6549	1,8854	131,593	0,3480	26,151

Constants for calculation of $P_{D\infty}$			
n_1 (25°)	n_1^2	A'	B'
1,3724	1,8835	0,3474	26,176

In Table 3 are given the results of measurements of the dielectric constant (ϵ), the density ($\underline{d}$), and the refractive index (n_D) of solutions of the hexaalkyl derivatives of disiloxane in n-hexane for various concentrations of the dissolved material, expressed in mole fractions (C_2).

From the data in Tables 2 and 3 the constants were calculated that were necessary for the calculation of the dipole moments by Hederstrand's method. These constants are given in Table 4.

For the series of compounds $\alpha\epsilon$, βd_1, and γn_1^2 are not related linearly to the concentration, therefore it was necessary to extrapolate to zero concentration. For this purpose curves were constructed for $\epsilon = f_1(c_2)$, $d = f_2(c_2)$, and $n_2 = f_3(c_2)$, and tangents were drawn at the point $c_2 = 0$. The tangent of the angle of slope of the tangent line to the axis of concentration also gave the value sought.

As indicated above, in the literature there are data only on the dipole moment of hexamethyldisiloxane. The dipole moment of this compound measured in benzene was 0.80 D [2]. According to other data [3], the dipole moment of hexamethyldisiloxane measured in benzene at 30° is 0.79 D. These values agree well with that obtained by us, 0.78 D.

The values of the dipole moments of the hexaalkyl derivatives of disiloxane given in Table 4 show that the Si–O bond is strongly polar. This is the result of the considerable difference in the electronegativity of Si and O.

The observed decrease in the magnitude of the dipole moment of the molecules containing the ethyl, propyl, and butyl radicals can be explained, apparently, by an increase in the valence angle elicited by the pushing apart of the bulky groups.

TABLE 3

Experimentally Found Values of ϵ, d, and n_D For Solutions of Hexaalkyl Derivatives of Disiloxane in n-Hexane

C_2	ϵ_{12}	d_4^{25}	n_D^{25}	C_2	ϵ_{12}	d_4^{25}	n_D^{25}
Hexamethyldisiloxane in n-hexane				Hexapropyldisiloxane in n-hexane			
0	1,8854	0,6549	1,3724	0	1,8854	0,6549	1,3724
0,0206	1,8956	0,6585	1,3726	0,0197	1,9032	0,6659	1,3767
0,0353	1,9029	0,6607	1,3727	0,0346	1,9182	0,6725	1,3799
0,0499	1,9076	0,6633	1,3728	0,0496	0,9334	0,6788	1,3824
Hexaethyldisiloxane in n-hexane				Hexabutyldisiloxane in n-hexane			
0	1,8854	0,6549	1,3724	0	1,8854	0,6549	1,3724
0,0201	1,9010	0,6635	1,3755	0,0196	1,9108	0,6684	1,3781
0,0351	1,9107	0,6699	1,3776	0,0348	1,9294	0,6770	1,3822
0,0499	1,9210	0,6755	1,3795	0,0486	1,9381	0,6858	1,3856

TABLE 4

Constants for the Calculation of the Dipole Moments of the Hexaalkyl Derivatives of Disiloxane by Hederstrand's Method

Compound	M_2	$\alpha\varepsilon_1$	βd_1	P_∞	γn_1^2	$P_{D\infty}$	P_{op}	$\mu \cdot 10^{18}$
$(CH_3)_3SiOSi(CH_3)_3$	162,39	0,4958	0,168	61,8	0,022	49,3	12,5	0,78
$(C_2H_5)_3SiOSi(C_2H_5)_3$	246,55	0,772	0,427	86,4	0,434	77,5	8,9	0,66
$(C_3H_7)_3SiOSi(C_3H_7)_3$	330,71	0,948	0,640	110,6	0,599	101,3	9,3	0,67
$(C_4H_9)_3SiOSi(C_4H_9)_3$	414,88	1,215	0,6775	145,1	0,830	134,9	10,2	0,71

LITERATURE CITED

[1] A. V. Topchiev, N. S. Nametkin, and V. I. Zetkin, Proc. Acad. Sci. 99, 551 (1954).

[2] Y. Kurita and M. Kondo, Bull. Chem. Soc. Japan 27, 160 (1954).

[3] H. Freiser, M. Fagel, and J. Speier, J. Am. Chem. Soc. 75, 2824 (1953).

[4] R. Guillien, Radium 29, 1 (1940).

[5] F. C. DeVos, Rec. Trav. Chim. 69, 1157 (1950).

[6] R. O. Sauer and D. J. Mead, J. Am. Chem. Soc. 68, 1794 (1946).

[7] G. Hedestrand, Zs. Phys. Chem. (B) 2, 429 (1929).

Received May 13, 1958

CONDENSATION OF THE ACETAL OF β-CYCLOCITRAL WITH 1-ETHOXYISOPRENE

Academician I. N. Nazarov and Zh. A. Krasnaia

A method of synthesis developed by us previously for unsaturated aldehydes of the isoprenoid type, which was based on the condensation of acetals with 1-alkoxydienes [1], permits lengthening the isoprenoid carbon chain by five or ten carbon atoms at one time.

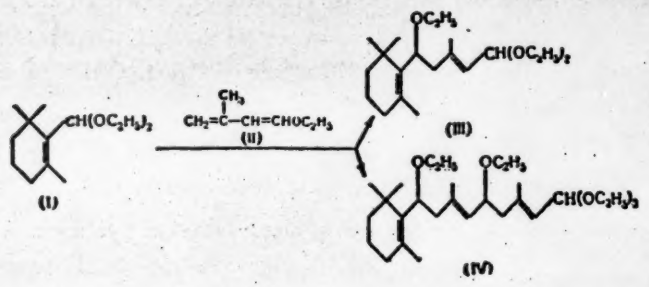
By the use of this method such polyenals were prepared as octatrienal, dehydrocitral, farnesynal, etc., and a series of α, β-unsaturated ether-aldehydes also were synthesized: 4-ethoxycitral, 4,8-diethoxyfarnesal, etc.

This interesting reaction opens a simple way for the synthesis of β-ionolideneacetaldehyde and the aldehyde of vitamin A, and with this objective we investigated the condensation of the acetal of β-cyclocitral (I) with 1-ethoxyisoprene (II).

The previously unknown acetal of β-cyclocitral (I) was obtained by the action of orthoformic ester on β-cyclocitral.

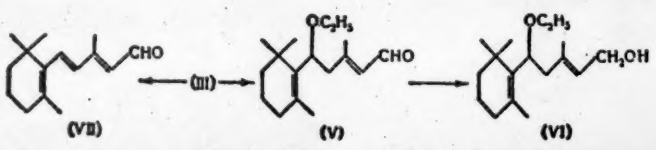
In the presence of zinc chloride the condensation of the acetal of β-cyclocitral (I) with ethoxyisoprene (II) results in a mixture of the ether-acetals of the C_{15} aldehyde (III) and the C_{20} aldehyde (IV) with yields of 44.6 and 25% respectively, these products being easily separated by vacuum distillation.

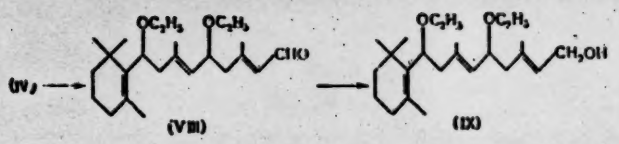
The best yields of the ether-acetals (III) and (IV) were obtained with a 2:1 ratio of the acetal (I) and the ethoxyisoprene (II) and a temperature of 40-45°.



By hydrolysis of the ether-acetal (III) with dilute orthophosphoric acid, we smoothly obtained ethoxydihydro-β-ionolideneacetaldehyde (V), the reduction of which with sodium borohydride yielded the corresponding ethoxydihydro-β-ionolidenethyl alcohol (VI).

From the ether-acetal (III) there was obtained in satisfactory yield, by the action of orthophosphoric acid in dioxane, the β-ionolideneacetaldehyde (VII).





By similar conversions from the ether-acetal (IV) it was possible to accomplish the synthesis in good yields of the diethoxybisdihydroaldehyde of vitamin A (VIII) and diethoxybisdihydrovitamin A (IX), which are important intermediate products for the synthesis of vitamin A and which may have biological interest in themselves.

EXPERIMENTAL

Diethylacetal of β-cyclocitral (I). A solution of 104 g of β-cyclocitral (b. p. 93-95°/10 mm; n^{20}_D 1.4958), 130 g of orthoformic ester, and 14.3 mg of p-toluenesulfonic acid in 48 ml of abs. ethyl alcohol was allowed to stand for 3 days at room temperature, and after neutralization with sodium ethylate the mixture was distilled in vacuo.

As a result of 2 distillations the following fractions were obtained:

1st fraction (67-70°/36 mm, n^{17}_D 1.3960), 70 g orthoformic ester;

2nd fraction (93-104°/10 mm, n^{19}_D 1.4880) 62 g starting β-cyclocitral;

3rd fraction (104-112°/10 mm, n^{17}_D 1.4710) 58 g mixture of β-cyclocitral and its acetal.

The 3rd fraction obtained from several experiments (103 g) was distilled on a fractionating column with a glass cap. After removal of the β-cyclocitral the residue was distilled from a Favorskii flask and in this way 32.5 g of the acetal of β-cyclocitral (I) was separated with b. 0. 105-107°/7 mm, n^{20}_D 1.4615.

Found %: C 74.43, 74.47; H 11.40, 13.41. $C_{14}H_{26}O_2$. Calculated %: C 74.29; H 11.58.

From the acetal (I) a semicarbazone was obtained with m. p. 164-166° (from ethanol), which gave no depression with the semicarbazone of β-cyclocitral.

Condensation of the acetal of β-cyclocitral (I) with ethoxyisoprene (II). To a mixture of 40 g (0.177 mole) of the acetal (I) and 4 ml of 10% zinc chloride solution in ethyl acetate was added slowly (in 3.5 hours) at a temperature of 42° and with stirring 10 g (0.089 mole) of ethoxyisoprene (II). Then the mixture was stirred for 1 hour and 15 min. more at a temperature of 42-45°, after which it was cooled, diluted with ether, washed with 5% sodium hydroxide solution, then with water, dried, and distilled. As a result of 2 fractional distillations in vacuo the following fractions were obtained:

1) 24.7 g of the starting acetal (I) with b. p. 68-73°/0.7 mm, $n^{19.5}_D$ 1.4670;

2) 10 g (yield • 44.6%) of the ether-acetal of the C_{15} aldehyde (III) as a colorless liquid with b. p. 105-107°/0.08 mm, n^{20}_D 1.4740, d^{20}_4 0.9466, MR found 100.5, calculated 100.97.

Found %: C 74.13, 74.16; H 11.17, 11.03. $C_{21}H_{38}O_3$. Calculated %: C 74.50; H 11.32.

3) 7.4 g (yield • 25%) of the ether-acetal of the C_{20} aldehyde (IV) as a yellowish, viscous liquid with b. p. 152-156°/0.07 mm, n^{20}_D 1.4828.

Found %: C 74.92, 75.04; H 11.06, 11.15. $C_{28}H_{50}O_4$. Calculated %: C 74.61; H 11.18.

Ethoxydihydro-β-ionolideneacetaldehyde (V) (3-methyl-5-ethoxy-5-(2,6,6-trimethylcyclohexen-1-yl-1) penten-2-al). A mixture of 10 g of the ether-acetal (III), 25 ml of 5% orthophosphoric acid, and 5 ml of ethyl alcohol was stirred at 95° in a current of nitrogen for 1 hour. After the reaction mixture had been cooled, ether was added, the organic layer was separated, washed with sodium bicarbonate solution, then with water, dried with sodium sulfate, and distilled in vacuo. 6.2 g of the ether-aldehyde (V) was obtained with b. p. 98-99°/0.07 mm, $n^{21.5}_D$ 1.5045.

• Yield calculated on acetal (I) going into the reaction

λ_{max} (in ethanol) 240 mμ (log ε 4.086).

Found %: C 77.45, 77.18; H 10.88, 10.82. $C_{17}H_{28}O_2$. Calculated %: C 77.21; H 10.67.

The 2,4-dinitrophenylhydrazone of the ether-aldehyde (V) was obtained as a mixture of geometric isomers with m. p. 137-145° (after 2 recrystallizations from ethanol).

λ_{max} (in heptane) 368 mμ (log ε 4.14), 290 mμ (log ε 3.79), 256 mμ (log ε 4.107).

Found %: C 62.01, 62.29; H 7.29, 7.01; N 13.02, 12.58. $C_{23}H_{32}N_4O_5$. Calculated %: C 62.13; H 7.26; N 12.6.

The semicarbazone of the ether-aldehyde (V) was obtained also as a mixture of geometric isomers with m. p. 153-161° (after recrystallization from 90% methanol).

Found %: N 13.28, 13.30. $C_{18}H_{31}O_2N_3$. Calculated %: N 13.07.

β-Ionolideneacetaldehyde (VII). A mixture of 2.5 g of the ether-acetal (III), 1 ml of 90% orthophosphoric acid, 20 ml of dioxane, and 6 ml of water was heated for 5 hours at 88-90° in a current of nitrogen in the presence of traces of hydroquinone. During the heating the dioxane, and water distilled off slowly; at the same time a 4:1 mixture of dioxane and water was added to the flask so that the volume of the reaction mixture remained constant. The reaction mixture was cooled, poured into ice water (30 ml), and the product was extracted with ether. The ethereal extract was washed with sodium bicarbonate solution, then with water, dried, and distilled. 1.4 g of an orange-yellow liquid was obtained with b. p. 91-97°/0.09 mm.

The product obtained, admixed with 2 ml of 90% orthophosphoric acid, 20 ml of dioxane and 6 ml of water, was again subjected to the above-described operation. After distillation, 0.7 g was obtained of a material with b. p. b. p. 91-94°/0.09 mm, which was β-ionolideneacetaldehyde (VII), the 2,4-diphenylhydrazone of which melted at 195-196° (from a mixture of ethanol and ethyl acetate).

λ_{max} (in ethanol) 319 mμ (log ε 4.191), 408 mμ (log ε 4.599).

Found %: C 63.35, 63.18; H 6.50, 6.48; N 14.30, 14.31. $C_{21}H_{25}O_4N_4$. Calculated %: C 63.31; H 6.53; N 14.07.

According to the literature data, the 2,4-dinitrophenylhydrazone of β-ionolideneacetaldehyde melts at 199-201°, λ_{max} (in ethanol) 260 mμ (log ε 4.1987), 320 mμ (log ε 4.1461), 400 mμ (log ε 4.5635) [2]; at 198-200°, λ_{max} 405 mμ (log ε 4.5966) [3].

Ethoxydihydro-β-ionolidenethyl alcohol (VI) (3-methyl-5-ethoxy-5-(2,6,6-trimethylcyclohexen-1-yl-1) penten-2-ol). To a solution of 2.2 g of the ether-aldehyde (V) in 18 ml of 96% ethyl alcohol, with stirring and at a temperature of 10-12°, was added 370 mg of sodium borohydride (85% content) over a period of 1 hour in a current of nitrogen.

Then the mixture was stirred for 1 hour more at the same temperature and left overnight at room temperature. The excess sodium borohydride was decomposed with acetic acid (7-8 drops), the alcohol was distilled off in a slight vacuum, water and ether were added to the residue, the ether layer was separated, and the aqueous layer was extracted twice with ether. The combined ether extract was washed with water, dried with calcined magnesium sulfate, and distilled.

1.65 g of ethoxydihydro-β-ionolidenethyl alcohol (VI) was obtained with b. p. 87-88°/0.025 mm, n^{20}_D 1.4943.

Found %: C 76.60, 76.85; H 11.49, 11.44. $C_{17}H_{30}O_2$. Calculated %: C 76.66; H 11.35.

Number of active hydrogens found: 0.99; 1.06.

Diethoxybisdihydroaldehyde of vitamin A (VIII) (3,7-dimethyl-5,9-diethoxy-9-(2,6,6-trimethylcyclohexen-1-yl-1)nonadien-2,6-al). A mixture of 13.7 g of the ether-acetal (IV), 29 ml of 5% orthophosphoric acid, and 6 ml of ethyl alcohol was stirred in a current of nitrogen at 95° for 1 hour and treated as described above for the preparation of the ether-aldehyde (V). 9 g of the ether-aldehyde (VIII) was isolated with b. p. 155-157°/0.1 mm, n^{20}_D 1.5070.

λ_{max} (in ethanol) 240 mμ (log ε 4.123), 340 mμ (log ε 3.677).

Found %: C 76.92, 76.91; H 10.55, 10.54. $C_{24}H_{40}O_3$. Calculated %: C 76.52; H 10.70.

It was not possible to obtain the 2,4-dinitrophenylhydrazone and the semicarbazone of the ether-aldehyde (VIII) in the crystalline condition.

Diethoxybisdihydrovitamin A (IX) (3,7-dimethyl-5,9-diethoxy-9-(2,6,6-trimethylcyclohexan-1-yl-1) nonadien-2,6-ol). To a solution of 3.1 g of the ether-aldehyde (VIII) in 18 ml of 97% ethyl alcohol, at a temperature of 10-12° and with stirring, was added over a period of 2 hours 370 mg of sodium borohydride. After treatment as described above and distillation, 2.4 g of diethoxybisdihydrovitamin A (IX) was obtained as a viscous, almost colorless liquid with b. p. 143-145°/0.025 mm, n^{20}_D 1.5020.

Found %: C 75.85, 75.90; H 11.11, 11.20. $C_{24}H_{42}O_3$. Calculated %: C 76.12; H 11.18.

Number of active hydrogens found: 0.85; 0.85.

LITERATURE CITED

[1] L. N. Nazarov and Zh. A. Krasnaia, Proc. Acad. Sci. 118, 4, 716 (1958).*

[2] H. O. Huisman, Rec. Trav. Chim. 69, 851 (1950).

[3] C. D. Pobeson and J. D. Cawley, British Patent No. 701,807 (1954); Chem. Abstr. 49, 6308 (1955).

N. D. Zelinskii Institute of Organic Chemistry
of the Academy of Sciences, USSR

Received May 13, 1958

* Original Russian pagination. See C. B. Translation.

SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR.
GDI	Water Powet Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab.-Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Meteorology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

Note: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. - Publisher.

AR-2-1-V
08:00 05/08/2015